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AMERICAN

CHEMICAL JOURNAL.

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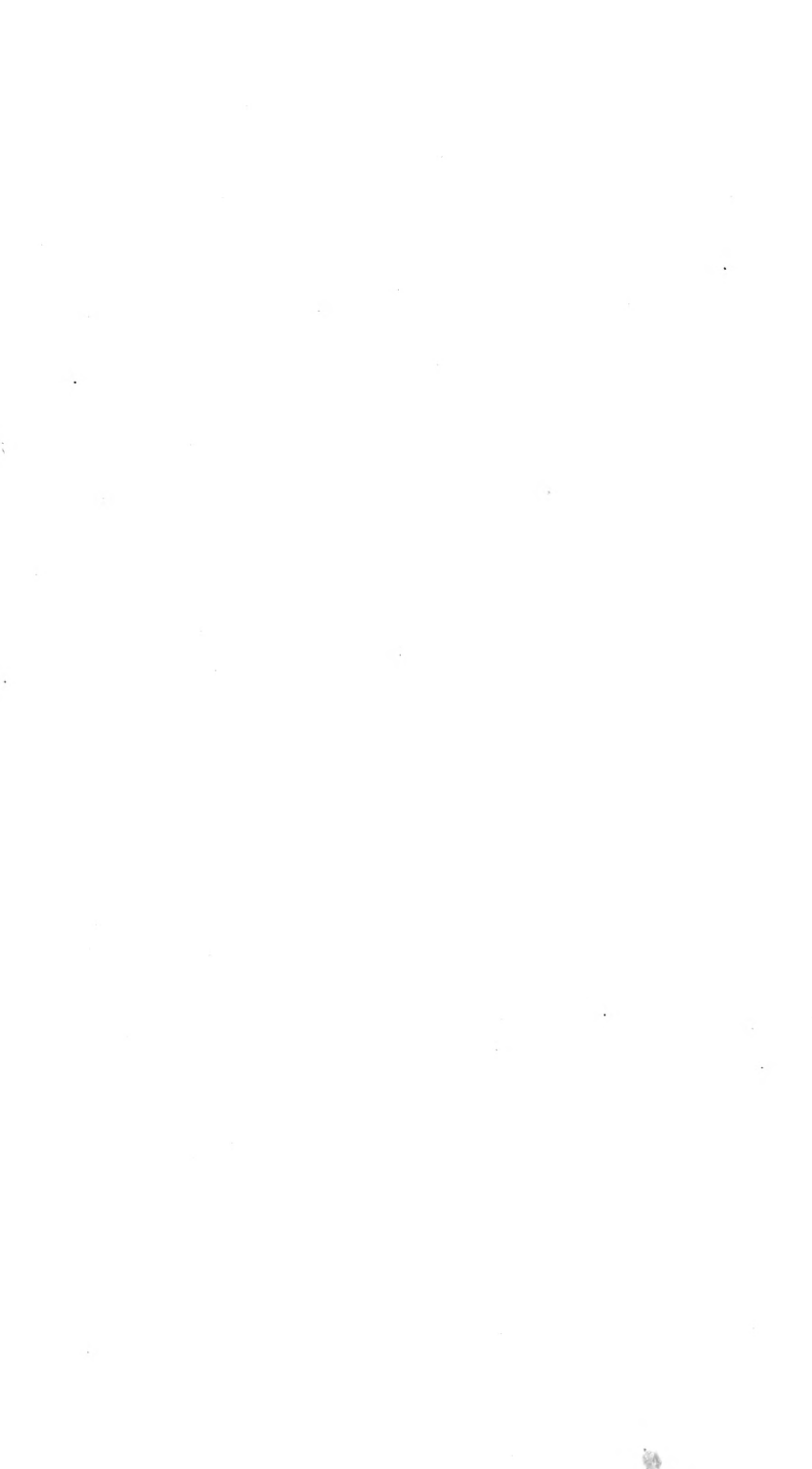
IRA REMSEN

PROFESSOR OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY.

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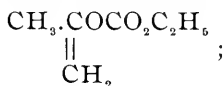
AMERICAN CHEMICAL JOURNAL.

Contributions from the Laboratory of General Chemistry, University of Michigan.

I. ON THE ACTION OF CHLORCARBONIC ESTER ON SODIUM ACETONE.

BY PAUL C. FREER.

Some time ago I published a short preliminary notice¹ on this subject (in conjunction with Geo. O. Higley). In this paper we demonstrated that a neutral oil which, on distillation, could be separated into two portions (one boiling between 125° and 135° and one above 200°) is to be obtained as a product of the reaction. At that time we isolated from the lower fraction, a colorless fluid, with a boiling-point of approximately 130°, and as the analyses, as well as the vapor density determinations of this body gave us numbers which agreed very well with those calculated for aceto-acetic ester, and as, furthermore, it did not react with phenylhydrazine and yielded carbon dioxide, acetone, and alcohol on saponification, we felt justified in assuming that the substance in question had a constitution to be expressed by the formula



¹ This Journal, 13, 322.

There was one circumstance, mentioned at the time in connection with this work, which seemed to demand further investigation, and this was the fact that, although the numbers obtained for carbon agreed perfectly with the theory, the hydrogen was always found to be somewhat too high. It was with the purpose of finding an explanation of this discrepancy that I resumed the research with the larger quantities of sodium acetone, and the better apparatus which were subsequently at my disposal, and, in so doing, I discovered that the previously described oil, with a boiling-point of 130° , was in reality a mixture of several bodies, all of which distill at about the same temperature. It is impossible to accomplish the perfect separation of these bodies by fractional distillation, yet such a mixture would give analytical results in accordance with those detailed in the previous preliminary notice.

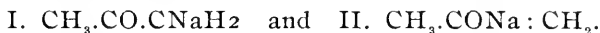
One fact, however, definitely appears as a result of the new experimental work, and this is that the greater portion of the various bodies which are obtainable as a result of the reaction between sodium acetone and chlorcarbonic ester is in reality the carbonic ester, the existence of which was previously assumed, and to which the formula $\text{CH}_3\text{.COCO}_2\text{C}_2\text{H}_5$ had



been assigned. Furthermore, it has never been possible to isolate either aceto-acetic ester, or the products of the reactions between the sodium derivative of the latter body and chlorcarbonic ester (acet-malonic ester or methin-tricarboxylic ester) from the substances which are produced,¹ so that no proof is obtainable that addition-products, in which the substituting radicle is attached to carbon, are here formed, (as is the case in the action of benzoyl chloride on sodium acetone). The behavior of this body toward chlorcarbonic ester, therefore, furnishes definite proof that the sodium in sodium acetone is

¹ Once only could I obtain from the higher-boiling portions of the products of the reaction an oil which gave a violet coloration with ferric chloride. As I suspected the presence of aceto-acetic ester, I extracted with ten per cent. sodium hydroxide solution, neutralized the extract at once, and then shook the resulting fluid out repeatedly with pure ether. On evaporating the solvent, only traces of an oil (which colored ferric chloride), remained. This substance was too small in quantity to permit of identification, but it most probably was aceto-acetic ester.

joined to oxygen only. It follows from the above, however, that the mono- and dibenzoyl-acetone (which I formerly obtained by the action of sodium acetone on benzoyl chloride) were derived from intermediary addition-products, as I assumed in my paper on that subject.¹ The only other view which was in accord with the facts previously observed was that *two* sodium derivatives of acetone existed, with the following structures :



Of these the first would give C, the second O substitution products when treated with organic halides. This interpretation of the facts is now definitely contradicted by the behavior of sodium acetone toward chlorcarbonic ester, while, at the same time, this work furnishes strong support to the theory of processes of addition, which is at the present time accepted by many chemists. As mono- and dibenzoyl acetone *must* have resulted from the decomposition of foregoing addition-products, it follows that in the case of aceto-acetic ester, the formation of C substituted bodies should also be ascribed to identical processes.

EXPERIMENTAL PART.

Preparation of the Initial Product.

Three grains of sodium (in the form of the finest wire) are placed in a flask, covered with absolute ether and then converted into sodium acetone, according to the method described in my former paper,² air being at the same time rigidly excluded by means of a current of pure hydrogen. After all of the sodium has disappeared, somewhat less than the calculated quantity of chlorcarbonic ester is gradually run in through a dropping funnel. A violent reaction begins at once, sodium chloride apparently being formed, while the process may at times become so energetic as to necessitate the cooling of the flask by means of ice-water. After all of the chlorcarbonic ester has been added, the container is tightly stoppered while a current of hydrogen is passing into it, and it is then allowed to stand in a warm place for about ten days

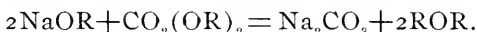
¹ This Journal, **15**, 604.

² *Ibid*, **15**, 588.

By this time the white salt, which has been formed, has almost entirely settled. The latter is then filtered off, washed with absolute ether, and it, as well as the straw-colored filtrate, is preserved until the results of fifteen such processes can be worked up at the same time.

The Investigation of the Solid Product.

The solid, which separated during the above reaction, presumably was sodium chloride, and, indeed, acting on that supposition during the former work on this subject, it was thrown aside without further examination. Subsequently it occurred to me that this precipitate might not be as simple in composition as I had at first supposed, and on investigation, the analyses showed that at least 15 per cent. of the salt consisted of *sodium carbonate*, while a very small percentage (less than 2.5) was the sodium compound of an alcohol.¹ This rather surprising result shows that there must have been considerable decomposition, either of the chlorcarbonic ester used in the original reaction, or of the carbonic esters which were formed subsequently. This decomposition may be due to sodium hydroxide, which could have resulted from the action of water (formed by the condensation of acetone to phorone), in which event some free alcohol should be found among the products of the reaction; or it can have been caused by double decomposition taking place between the sodium-organic compounds and the carbonic esters which are produced:



If the latter change were to have taken place, then ethyl-isoacetone ether² might be expected to be formed, but, heretofore, I have not been able to prove the presence of this body. This fact need not exclude the possibility of its presence, however, for such an ether would, owing to its low boiling-point (62°), be most difficult to detect in the presence of the large amount of ethyl ether which is necessary for successful work with sodium acetone. It is very likely that both of the above changes take place simultaneously, for I have been

¹ Presumably sodium isopropylate, unacted on by the chlorcarbonic ester.

² The derivatives of methyl-vinyl alcohol; $\text{CH}_3.\text{COH}:\text{CH}_2$ (β -allyl alcohol) may perhaps best be termed derivatives of isoacetone, a nomenclature adopted by Claisen. *Ann. Chem. (Liebig)*, **277**, 169.

able to isolate a considerable quantity of free alcohol from the fluid products of the reaction, yet this alcohol is not of a sufficient quantity to account for all of the sodium carbonate which is produced. The presence of sodium carbonate, mixed with the salt which was formerly supposed to be sodium chloride, shows that it is possible to have had similar decompositions in other cases where chlorcarbonic ester has reacted with sodium-organic compounds (so, for example, with sodium aceto-acetic ester) so that those precipitates which heretofore have been considered as being nothing but sodium chloride, may, in reality, also contain the carbonate, while the formation of the latter body may naturally influence the entire reaction. Another possible source of the sodium carbonate may be found in the decomposition of chlorcarbonic addition-products to sodium acetone (*i. e.* aceto-acetic ester or its derivatives) and this fact may account for the entire absence of such bodies among the substances to be isolated.

The Fluid Products of the Reaction.

The straw-colored, filtered liquid was first roughly divided into two parts by distillation, one portion boiling up to 110° and the second above this point. A considerable quantity of hydrochloric acid separates during this operation, while the fluid, which remains, turns to a dark-green color.¹ I was also able to isolate a certain amount of ethyl alcohol from the

¹ The hydrochloric acid is formed only during the process of distillation. It could not have been present before, otherwise it would have decomposed the sodium carbonate. In spite of the fact that less than the theoretical quantity of chlorcarbonic ester is used during the reaction, the latter body is always to be found among the distillation products. This fact is probably due to the saponification of a certain amount of the carbonic esters which are formed. This saponification would result in the removal of a portion of the sodium and the formation of sodium carbonate. The excessive chlorcarbonic ester can now, on distillation, react with the alcohol which has been set at liberty, thus forming carbonic diethyl ester and hydrochloric acid, while the latter body adds itself to the unsaturated organic substances which are present, to be once more separated when the latter are heated. As a result, carbonic diethyl ester should be among the products of the reaction, and, indeed, as will be shown below, I have succeeded in isolating a considerable quantity of that body from the oil boiling between 125° and 135° . This formation of hydrochloric acid is of importance because the production of the condensation products of acetone is to be attributed in part to its action. Equally complicated results have also been obtained in other reactions between chlorcarbonic esters and sodium alcoholates. Röse, *Ann. Chem. (Liebig)*, **205**, 227. Another explanation for the hydrochloric acid can be found in the decomposition of addition-products; this will be discussed subsequently.

lower fraction. This was accomplished by means of careful distillation with a dephlegmator, extraction with water of the part passing over between 68° and 85° , saturation of the solution with potassium carbonate, separation of the organic liquid, treatment with sodium bisulphite solution, etc., according to the usual methods. No isopropyl alcohol was present, as was proved by analyses which were made. The oil passing over between 85° and 110° consisted, for the most part, of unchanged chlorcarbonic ester and of the bodies belonging to the next higher fraction.

The part boiling above 110° was placed in contact with a little water, and was then allowed to stand for several hours. During this time crystals of hydrated pinacone separated in considerable quantity. The presence of free pinacone must either be attributed to reactions similar to those which produced the free ethyl alcohol; or else it is to be referred to the action of an acid, which later is formed as a result of previous processes of addition (as is the case in the work with benzoyl chloride¹), but, as was mentioned before, addition-products or their derivatives are not to be found among the final bodies.² After the pinacone was filtered, the clear liquid was extracted repeatedly with a 10-per cent. sodium hydroxide solution,³ washed several times with water, dried over calcium chloride, and then all that would pass over below 150° , distilled off.

Investigation of the Low-Boiling Oil.

The portion of the whole oil which passed over between 110° and 150° was carefully and repeatedly fractioned, and finally separated as follows:

112° – 126° (contains considerable $\text{ClCO}_2\text{C}_2\text{H}_5$); 126° – 128° : 8 grams; 128° – 129° : 8 grams; 129° – 130° : 24 grams; 130° – 132° : 16 grams; 132° – 137° : 8 grams.⁴

¹ This Journal, **15**, 604.

² The presence of sodium pinaconate among the products of the action of sodium on acetone was proven in this Journal, **15**, 592.

³ The alkaline solution was instantly neutralized with sulphuric acid and then extracted repeatedly with pure ether. On evaporating the solvent, nothing but a few crystals of pinacone remained. Only once did I succeed in getting about 0.8 of a gram of an oil which colored ferric chloride solution and which, presumably, was aceto-acetic ester. Acid organic substances are, therefore, not formed in any quantity.

⁴ The above amounts are not exact, but simply approximate.

All of these portions contained chlorine, and in consequence of this fact, they were afterwards separately distilled over small pieces of sodium until all of the halogen was removed. They were then carefully refractioned, but it was impossible to isolate a body with a perfectly constant boiling-point from any of the portions. For example, the fraction passing over between 129° and 130° would, on repeated distillation, yield a small quantity of an oil boiling between 124° and 128° as well as a few drops of a substance which would not pass over under 150° , and even if a product which, when working with larger quantities distilled within 0.5° , was refractioned by itself, no other result could be obtained.¹ Indeed, nothing else is possible under the circumstances, for this oil is, as I will demonstrate below, an inseparable mixture of several bodies, which, furthermore, interact, the one with the other, when they are heated. This fact is entirely in accord with the discovery of R  se,² who found that a mixture of chlorcarbonic methyl or ethyl ester, with an alcohol of higher molecular weight, was changed *even at ordinary temperatures* in such a way that the alcohol of lower molecular weight was expelled from its compounds by the one with the higher; so that for example carbonic dipropyl ester and methyl alcohol are produced from carbonic methyl propyl ester and propyl alcohol, although some of the original bodies still remained after all interaction was complete.

The product of the reaction between chlorcarbonic ester and sodium acetone, after being purified and fractioned as detailed above, is perfectly colorless and possesses a strong ethereal odor (reminding one of that of carbonic diethyl ester); it does not react with phenylhydrazine, even after standing for a number of hours, and it takes up bromine at once and in the cold, without liberating hydrobromic acid. When warmed for a short time with baryta water, or for a longer

¹ I have endeavored, by using the most varied means of purification, to obtain a product with a perfectly constant boiling-point, but without success. So, for example, I have treated the crude oil with phenylhydrazine until no further reaction could be noticed; have then distilled the mixture so obtained twice in a current of steam; and have finally fractioned this nearly pure product by the same means. I have also distilled the oil from perfectly pure phenylhydrazine, at a pressure of 30 mm., but could observe no difference in the result.

² Ann. Chem. (Liebig), **205**, 240.

time with hydrochloric acid, it is completely broken down into carbon dioxide, ethyl alcohol, isopropyl alcohol, and *acetone*. This oil obviously is a mixture of carbonic esters *which yields acetone on saponification*, but in order to prove that at least a portion of this acetone *must have been present* in an isoacetone carbonic ester, it is necessary experimentally to fulfill the following three conditions:

I. The combustions must yield numbers which agree with those calculated for a mixture of carbonic esters, such as the one under discussion.

II. The amount of carbon dioxide which is obtainable on saponification must be so great as to exclude the possibility of having all of the acetone derived from a compound which is not a carbonic ester of isoacetone.

III. The quantity of acetone to be regained by saponification must be so large that, after considering the foregoing conditions, the theory that this acetone may have resulted from a body which is not an ester of carbonic acid, is excluded.

As the following details prove, these three conditions have, in reality, been experimentally realized.

I. It seems unnecessary to enumerate all of the analyses which were made, because the results of a series of preparations are in practical agreement; in the following table I have compiled the averages of a considerable number of determinations:

Calculated for:	Carbon, per cent.	Hydrogen, per cent.	Oxygen, per cent.
Carbonic diethyl ester: $\text{—C}_5\text{H}_{10}\text{O}_3$	50.84	8.47	40.69
“ ethyl-isoacetone ester: $\text{—C}_6\text{H}_{10}\text{O}_3$	55.38	7.69	36.93
“ di-isoacetone ester: $\text{—C}_7\text{H}_{10}\text{O}_3$	59.01	7.04	33.95
“ ethyl-isopropyl ester: $\text{—C}_6\text{H}_{12}\text{O}_3$	54.53	9.00	36.47
“ di-isopropyl ester: $\text{—C}_7\text{H}_{14}\text{O}_3$	57.53	9.58	32.99
Found for the fractions:			
125.5° to 126.5°	53.48	8.55	37.97
129° to 130°	55.40	8.23	36.37
131° to 132°	55.35	8.93	35.72
132° to 134°	56.17	9.01	34.82
136° to 138°	57.64	9.16	33.20

An examination of the above table shows that the percentages of carbon and hydrogen increase as the boiling-point advances, yet all of the numbers are undoubtedly such as would

be obtained from a mixture of the above carbonic esters. The only other class of bodies which are possibly present in the oil under discussion (and which would not react with phenylhydrazine, while possessing the proper boiling-point) would be reduction-products or esters of mesityl oxide, and such substances would yield 20 per cent. more carbon and 4 per cent. more hydrogen than the quantities in reality obtained.¹ The analyses of the fraction 129° to 130° (when purified with the greatest care) agree quite well with the theory for carbonic ethyl-isoacetone ester (with the exception that the hydrogen is 0.6 per cent. higher than the amount calculated for such a body) and the vapor density (calculated 4.5; found 4.44) is also in accord with the view that this portion of the oil contains the expected substance in a nearly pure state.

II. As the analytical data agree with those numbers which should be obtained, the next question to be decided is whether the experimental results are also in accord with the second of the above conditions. The best method for determining the relative quantity of carbon dioxide which is present in the body under discussion, was found to be in saponification by means of baryta water. A small quantity of the oil was weighed in a glass bulb, which was drawn to a point and afterward fused at the tip. This bulb was heated to 110° in a sealed tube with a slight excess of baryta water, the reaction being complete after about one-half an hour. After opening the tube, the barium carbonate was filtered, washed with boiling water, dissolved in dilute hydrochloric acid, reprecipitated with ammonium carbonate, again filtered into a Gooch crucible and finally weighed, after drying at 120°. The quantity of carbon dioxide to be obtained varied somewhat for the different fractions. It was 32 per cent. for 128°, and 33.7 per cent for 130°-132°. All of the determinations were in practical accord. The calculated amounts of carbon dioxide are as follows:

I. For $\text{CO}(\text{OC}_2\text{H}_5)_2$; CO_2 per cent. 37.28.

¹ Some analyses vary from the numbers given above, indeed the carbon may be as high as 59 and the hydrogen as high as 10.2 per cent. The cause of this difference will be given below. A reduction-product of mesityl oxide, if decomposed by hydrochloric acid, would certainly have to yield isopropyl alcohol. The latter body is not among the saponification-products of the lower fractions.

2. For $\text{CO}(\text{OC}_3\text{H}_5)_2$; CO_2 per cent. 30.98.
3. For $\text{CO}(\text{OC}_3\text{H}_5)(\text{OC}_2\text{H}_5)$; CO_2 per cent. 33.84. (Found 33.7 per cent.)¹
4. For $\text{CO}(\text{OC}_3\text{H}_5)(\text{OC}_3\text{H}_7)$; CO_2 per cent 30.55.

The above figures demonstrate that the quantity of carbon dioxide is also in full accord with the theory. The amount of acetone to be obtained by saponification must be very small indeed if, considering the high percentage of carbon dioxide, it is to be present in any other form than as a carbonic ester of isoacetone. As will be seen from the above numbers, the experimental data agree best with the body (3) which was theoretically expected to be present. Indeed one would be justified, after taking all of the previous work into consideration, in assuming its existence as a pure chemical individual in the fraction from 130° to 132° ; nevertheless it is also possible that we have here a mixture (for example of 1, 2, and 4, etc.) which would give the same analytical results. It is therefore necessary to bring further proof to bear on the subject, and, if possible, to fulfill the third of the above conditions.

III. In order to ascertain the percentage of acetone which is obtainable from the oil in question, the most convenient method was found to be in saponification by means of dilute hydrochloric acid, and subsequent isolation of the organic bodies produced. About 15 grams of the oil (boiling-point 128°) were boiled for ten hours with an excess of 20-per cent. hydrochloric acid, with an inverted condenser the outer end of which was connected with a wash-bottle containing a little water, so as to prevent any possible escape of organic fluids. At the expiration of the above-mentioned time, the small quantity of unchanged oil was separated, the solution neutralized and distilled until no iodoform reaction could be obtained with the remainder in the flask. The distillate was then saturated with potassium carbonate, again fractioned, and this process

¹ The sealed tubes are slightly attacked when heated with pure baryta water, but this is scarcely the case with the determinations which were made, as only a slight excess of the reagent was used for saponification so that but little of the base was left to attack the glass. Nevertheless, I made blank determinations so as to ascertain the utmost quantity of insoluble material to be obtained in this way from baryta water and glass, and have deducted this amount from the carbon dioxide found, so as to find the *lowest possible limit*. Taking these experiments into consideration, the above numbers for carbon dioxide would be 30.8 and 32.5 per cent.

continued until the fluid was nearly anhydrous, when it was finally twice distilled from pieces of caustic potash. It then boiled between 60° and 80° . This liquid was now carefully mixed with a concentrated solution of sodium bisulphite, when the whole changed to a semi-solid mass of acetone sodium bisulphite. This was filtered off, the filtrate distilled from sodium carbonate, and the distillate again treated as above until an anhydrous fluid was obtained which was entirely free from acetone. This liquid, when perfectly free from water, boiled at 78° and analyses proved it to be pure *ethyl alcohol*. The quantity of ethyl alcohol was found to be *less than one-half* of the total organic matter obtained by the process of saponification, the greatest care having been taken to prevent any loss during the various processes which have been detailed. The fraction boiling at 128° , therefore, breaks down into carbon dioxide, *ethyl alcohol*, and *acetone*, and the relative proportions of the latter are such that the oil in question must have contained the ethyl-isoacetone ester of carbonic acid.

The same methods of saponification and subsequent isolation of the products of the reaction were repeated with all of the other portions with successively increasing boiling-points; the fraction between 130° and 132° gave practically the same results, while that between 132° and 137° yielded *isopropyl alcohol* in addition to ethyl alcohol and acetone. I also made an attempt to determine, quantitatively, the amount of acetone obtainable from the oil boiling between 132° and 137° (in the other cases I had only decided on the relative proportion of this substance from the difference between the quantity of alcohol and the total anhydrous organic liquid) and found the same to be, at the very least, 30 per cent. of the whole.¹

If all of the results which have been detailed above are

¹ It is my experience that the amount of acetone which is present in a mixture of that body with ethyl and isopropyl alcohol, is not accurately determinable by any of the methods at present in use. In attempting to separate the acetone by the sodium bisulphite reaction, the loss is so great, owing to the solubility of the compound formed and to its decomposing when exposed to the air, that not even approximate results are obtainable. On the other hand the ammonium iodide, ammonia, and iodine reaction ceases before all of the acetone is converted into iodoform. It is possible that, in the future, I may be able to develop a method which will yield good results. As matters now stand, the above 30 per cent. represents less than the real quantity of acetone.

taken into consideration at the same time, the conclusion becomes inevitable that at least a portion of the acetone must be present in the original oil as carbonic ethyl isoacetone ester, for, even if we assume an extreme case, *i. e.*, that we are here dealing with a mixture of carbonic diethyl ester and some reduction product or ester of mesityl oxide, so that all of the acetone obtainable by saponification might have been derived from the latter, then, with the same percentage of carbon and hydrogen found on analysis, the *proportion of carbon dioxide* would of necessity be much less than that which is really obtainable, for every trace of organic substance which is not present as an ester of carbonic acid, must, evidently, reduce the percentage of dioxide, so that the figures for the latter would fall below 30, when the amount of acetone is above that number. Indeed, the results which have so far been obtained would justify one in assuming that the fraction from 128° to 130° was in reality, the pure body having the formula, $\text{CH}_3\text{—COCO}_2\text{C}_2\text{H}_5$, did not some further experiments prove

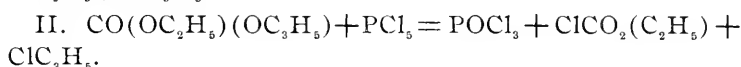
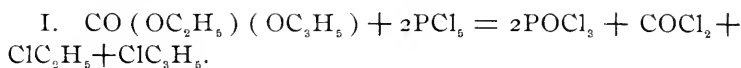
$$\begin{array}{c} \parallel \\ \text{CH}_3 \end{array}$$

that, contrary to my expectations, it is in all probability a mixture.

Decomposition of the Oil Between 130° and 131° with Phosphorus Pentachloride.

If the oil boiling between 130° and 131° is heated at 120°, for three or four hours, in a sealed tube with somewhat less than the calculated quantity of phosphorus pentachloride, a considerable pressure is produced, even if the container is opened while it is being cooled in a freezing-mixture. The gas which escapes is ethyl chloride. After opening the tube the entire liquid was poured into a fractioning flask and distilled. A considerable quantity of phosgene (boiling-point 8°) first passed over, the thermometer then rapidly rose to 23°, between which temperature and 25° a large proportion of a colorless oil was collected, while the remainder was divided into a part boiling from 95° to 105°, and one above the latter point. All of these fractions were now placed in contact with ice and allowed to stand until the carbonyl chloride and phosphorus oxychloride were decomposed. The second fraction

was afterward dried over calcium chloride and distilled. It now boiled constantly at 23.5° and on analysis gave 45.6 per cent. of chlorine (calculated for $\text{CH}_3\cdot\text{CCl}:\text{CH}_2$ (2-chlor-propene) 46.4 per cent. [B. p. 23.5°]). It is evident, from the above, that this organic halide is derived from the isoacetone of carbonic ethyl-isoacetone ester. The fraction 95° to 105° contained chlorcarbonic ester, so that the following reactions had taken place :



The most remarkable part of the reaction is, however, found in the fact that, after removal of the phosphorus oxychloride from the fraction above 105° , the latter proved itself to be a small quantity of pure *carbonic diethyl ether*. The most probable theory is that this body was present in the original oil¹ and that it was there formed by double decomposition between the various esters. It is possible, however, that this double decomposition took place during the continued heating in the presence of phosphorus pentachloride, as follows :



In either event, the carbonic diethyl ester, being the most stable organic body present, remains, in part, unchanged. If the first supposition (*i. e.* that the diethyl ester was present in the original oil) is true, then it is necessary to assume (in order to conform with the analytical data which were obtained) that carbonic di-isoacetone ester was also present. In all probability a small quantity of the latter body is formed during each fractionation. And this fact makes it intelligible why traces of low-boiling and high-boiling oils are present after each distillation, even of a product which had previously passed over within 0.5° .

Summary.

The fraction boiling between 130° and 131° is therefore, probably, nearly all carbonic ethyl isoacetone ester, mixed with

¹ It could not have been present in the chlorcarbonic ester used for the reaction, for I used a product which had been most carefully purified.

The High-Boiling Oil.

The portion of the original oil which boiled above 170° was mixed with pure phenylhydrazine, with the purpose of removing phorone, and other condensation-products of acetone.¹ After standing for some hours, this mixture was distilled in a current of steam and the yellow oil which passed over, washed with dilute hydrochloric acid, dried, and fractioned under diminished pressure; by this means a body boiling at 114° (30 mm.) can be isolated. The analytical results show that the formula to be assigned to this substance is $C_9H_{14}O_3$ while the vapor density (Hofmann's apparatus, vapor of aniline) indicates a molecular weight of 170. This oil has an ethereal odor which suggests that of mesityl oxide, and it is decomposed on boiling with hydrochloric acid into acetone, alcohol, and carbon dioxide.² These results agree with the theory that we have here an isomesityl-oxide-ethyl ester of carbonic acid, $(CH_3)_2C=CH-CO-CO_2C_2H_5$, and there is but little



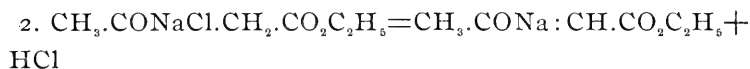
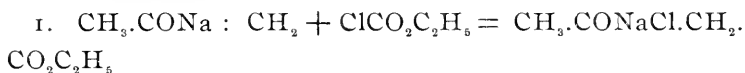
question that this body is in reality present. If this theory be correct, however, we must presuppose the existence of a sodium compound of mesityl oxide, and it will be my endeavor, in the future, to isolate this interesting and, presumably, very active substance.

It is interesting to observe that, among all of the products formed by the interaction of sodium acetone with chlorcarbonic ester there is none which indicates that processes of addition take place during the changes which go on. I had expected to find that aceto-acetic ether, or some of its derivatives would be formed in considerable quantity, just as I obtained mono- and dibenzoyl acetone under similar circumstances. The absence of such bodies in the final products does not, however, exclude their temporary formation altogether, for, as I pointed out in the introduction, the presence of sodium carbonate in the solid inorganic precipitate must be due to processes of decomposition. It is not impossible that sodium aceto-acetic ester is produced by the

¹ The latter substances form the larger proportion of the high-boiling oil.

² The amount of CO_2 given off was determined. Calculated $CO_2=25.8$, found, 24.2. The number is low because a slight remainder was undecomposed.

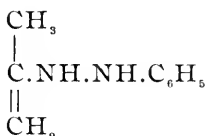
addition of chlorcarbonic ester to sodium acetone and by the subsequent separation of hydrochloric acid:



for the presence of free pinacone in the original products is abundant evidence of the action of some acid. It does not seem likely, however, that this sodium aceto-acetic ester would be so readily decomposed as to escape detection, although if it were to break down in the presence of alkalies, it would yield sodium carbonate, ethyl alcohol, and acetone. But sodium aceto-acetic ester might react with sodium acetone and the body or bodies so produced may be unstable. This question is obviously one which necessitates future investigation. So long as no processes, such as the above, can be clearly demonstrated, and so long as we can account for the presence of sodium carbonate by other and plausible means, we are not justified in assuming the existence of addition-products.

During the past year I have also endeavored to ascertain whether free acetone possesses the structure of an alcohol, just as its sodium compound has that of an alcoholic derivative, but the decision of this question is fraught with much greater difficulty. According to my experience, acetone reacts neither with acetyl chloride, benzoyl chloride, nor with acetic or benzoic anhydrides in such a manner that the iso-acetone esters of the acid in question are formed, as would be expected were acetone really an alcohol. Processes involving condensation, of course, take place to a certain extent. On the other hand, Kane has shown that a soluble barium compound (presumably of a constitution similar to that of the salts of ethyl-sulphuric acid) is obtainable by treating very cold acetone with sulphuric acid, with subsequent addition of barium carbonate.

Work done in my laboratory indicates that the so-called hydrazone of acetone has a structure represented by the formula



as the following considerations will show. When the above compound is mixed with considerably less than the calculated quantity of benzoyl chloride, (dissolved in dry toluene), a slow reaction sets in, and after some days a crystalline body separates. This body, insoluble in toluene, is the hydrochloride of the above hydrazo-compound. After this substance had been separated by filtration, it was noticed that the toluene solution had divided into two layers, the lower one of which was a thick oil. The upper layer was removed and carefully distilled in a vacuum. *It contains no acetone.* The lower thick oil was now repeatedly washed with ether, and each ethereal extract tested for acetone. Only traces of the latter substance were found. The ether was now removed from the thick oil, and the latter was then covered with dilute alcohol, containing a little hydrochloric acid, and then the whole gradually changed to a white crystalline solid, while the *alcoholic solution* contained a considerable quantity of acetone, which was isolated in the form of the sodium bisulphite compound. The crystalline solid, on recrystallization from absolute alcohol, melted at 178° , and proved to be dibenzoylphenylhydrazine. No matter how small the quantity of benzoyl chloride in proportion to the phenylhydrazine derivative of acetone (phenylhydrazo -2- propene), the same thick oil is always formed and the latter, with dilute alcohol or with water, always yields dibenzoylphenylhydrazine and acetone. There seems to be no doubt therefore, that the above thick oil is the dibenzoyl derivative of this hydrazo compound, and that, therefore, the phenylhydrazine derivative of acetone contains two hydrogen atoms, attached to nitrogen and replaceable by

benzoyl, its structure, therefore, is $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C.NH.NH.C}_6\text{H}_5 \\ || \\ \text{CH}_2 \end{array}$. This

fact does not, however, in my opinion prove that free acetones

in reality β -allyl alcohol, for the action of phenylhydrazine on acetone can easily be one of addition, with subsequent separation of water. The phenylhydrazine derivative of acetone is, furthermore, readily oxidized by means of mercuric oxide, when it is in gasoline solution and all air is excluded. The resulting product is a deep red oil which I have not, as yet, been able to crystallize. The phenylhydrazine derivative of benzophenone, which undoubtedly is a hydrazone, is much less readily produced than the corresponding acetone compound and is not readily oxidizable. I intend to give a more complete description of the above work at a future time, when I will also detail the results obtained with the phenylhydrazine derivative of acetophenone and enter into a discussion of the theoretical bearing of the reactions studied. I have also undertaken some work with acetoxime which

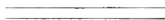
tends to show that the structure of that body is

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{C.NHOH.} \\ || \\ \text{CH}_2 \end{array}$$

This fact is especially brought out by the behavior of benzoyl-acetoxime. In the meantime, until the above investigations are prepared for complete publication, I beg my colleagues to allow me to reserve this field.

In closing I wish to take the opportunity of thanking Mr. R. R. Putnam for his valuable and energetic assistance in the work which has already been accomplished.

ANN ARBOR, *August*, 1894.



II.—THE ACTION OF METALS ON NITRIC ACID.

2. THE REDUCTION OF NITRIC ACID BY COPPER AND BY LEAD.

BY GEORGE O. HIGLEY.

A short time ago¹ I published (in conjunction with P. C. Freer) a preliminary notice on the action of copper on nitric acid, giving a few results of work done with an acid of the

¹ This Journal, 15, 71.

specific gravity 1.40. It was there shown that when the above strength of acid is used, the reduction-product is approximately pure nitrogen dioxide, and my work was confirmed by that of Montemartini,¹ who began his investigations in this field at about the same time. As my research was inaugurated before the article of that investigator appeared, and as, in several respects, it is conducted according to quite different methods, and as, moreover, his results, as a rule, account for more than 100 per cent. of the metal dissolved,² thus necessitating the theory that water takes part in the reactions between the metals and nitric acid, I have decided to continue my own research with the purpose of definitely settling the relation to be found between the nature and proportions of the reduction-products and the strength of acid used.

Early in the progress of this work several improvements were made in the apparatus described in the previous paper. The generating flask was changed as follows: Within the neck of an ordinary fractionating flask, of about 250 cc. capacity, was sealed a glass tube with an internal diameter of about five mm. and reaching nearly to the bottom of the flask; the upper end of this tube was connected, by means of a ground-glass joint, with the tube containing the acid. The stirring rod was discarded, it being thought that the liquid would be sufficiently agitated by the current of carbon dioxide constantly passing through it during solution of the metal. The joints, which were described as sealed with high-melting paraffin, were entirely replaced by those of ground glass. The nitrous and nitric oxides were collected in a gas tube over a 50-per cent. potash solution (previously saturated with nitrous oxide), and, after the removal of nitric oxide by means of an excess of oxygen, the residual gases were transferred to an explosion eudiometer over mercury, and their composition determined according to the usual methods.

The copper employed was chemically pure, and in the form of foil one-tenth mm. in thickness. The volume of acid taken was always increased with diminishing specific gravity, so that in no experiment was the quantity present less than ten times the amount requisite for the solution of the metal. Experiments

¹ *Gazetta Chimica Ital.*, **22**, 397.

² *Ibid.*, **22**, **1**., 250 and 277.

were usually undertaken in duplicate, and in each determination with an acid having a specific gravity of 1.25 or greater, two titrations of nitrosyl-sulphuric acid, and two nitrometer analyses were made.

Method of Stating Results.

In order to facilitate the comparison of results obtained under varying conditions, tables are given showing : 1. Temperature during solution. 2. Volume and specific gravity of acid. 3. Weight of nitrogen trioxide obtained from titration of nitrosyl-sulphuric acid contained in the Winkler tube. 4. Weight of trioxide from nitrometer analyses. 5. Weights¹ of trioxide and dioxide absorbed by the sulphuric acid with equivalent weights of metal. 6. Volumes of nitric and nitrous oxides, with respective metal equivalents. 7. Total metal dissolved and per cent. equivalent of metal found. These results are also finally given in the form of curves (p.26.), with the specific gravity of the acid as abscissae and the per cent. of metal equivalent, as ordinates.

The results of work done with copper are to be found in Table I. It will be observed that nitrogen is not given among the products of the reduction by copper of nitric acid of any degree of concentration. The small and fairly constant quantities of nitrogen found in the eudiometer after each explosion, were probably due to traces of air present in the carbon dioxide with which the oxides of nitrogen were swept forward, since blank tests maintained for two hours (the average time of a determination) resulted in the collection of appreciable quantities of air.

No nitrous oxide was obtained with acid solutions having a specific gravity greater than 1.15 ; the amount then increases with acid of specific gravity 1.10, and afterwards, contrary to expectation, it slightly decreases.

Nitric oxide was not found among the gases obtained by reduction of an acid of a specific gravity above 1.25 ; with greater dilution there is an increase of this gas, the course of which can best be followed from the corresponding curve in the appended diagram.

¹ For the method of calculation, see This Journal, 15, 78.

Nitrogen dioxide and trioxide in varying proportions are the sole products of reduction of nitric acid of specific gravity of 1.30 to 1.40.

While the amounts of trioxide, as determined by means of permanganate solution, are substantially constant, amounting to from 96.5 to 100 per cent. of the copper dissolved, the amount of trioxide from the nitrometer analyses shows a decided diminution with each successive dilution of acid, dropping from 315.7 milligrams (or nearly double the quantity obtained from the permanganate determination) to 68.5 milligrams, (an amount practically in agreement with the latter¹).

Apparently then, copper reduces strong nitric acid to nitrogen dioxide, and the latter, when it is expelled from the resulting solution by heat, passes over with but little decomposition to be absorbed by the sulphuric acid with the formation of nitrosyl-sulphuric and nitric acids. When such a solution of nitrogen dioxide is titrated by means of permanganate, there will be found one-half as great a quantity of trioxide as will be shown by the nitrometer.

In the reaction between nitric acid (specific gravity 1.35) and copper, the dioxide which is at first formed, undergoes further decomposition because the water which is present produces nitric acid and nitric oxide, the latter afterwards reacting with nitrogen dioxide so as to generate the trioxide. When copper is dissolved in nitric acid of still greater dilution, the decomposition of dioxide is increased to such an extent that when the specific gravity of 1.25 is reached it has entirely disappeared as such, as is proven by the practical equality of trioxide obtained in the permanganate and nitrometer analyses of the sulphuric acid (expt. 8) ; while, at the same time, 39 cc. of nitric oxide can be collected at this stage of the dilution.

With acids whose specific gravity diminishes below 1.25, the weight of trioxide steadily decreases, while the volume of nitric oxide advances.

¹ The relation between the nitrogen dioxide and trioxide is shown by the relation between the permanganate titration and the nitrometer results. For the method of calculation, see *loc. cit.*, p 78.

I. ACTION OF COPPER ON NITRIC ACID.

Experiment No.	Temperature.	Acid.		Winkler tube. Mgs. N_2O_3 .	Nitrometer. Mgs. N_2O_3 .	Nitrogen dioxide. Mgs.	Equivalent metal. Mgs.	Nitrogen trioxide. Mgs.	Equivalent metal. Mgs.	Nitric oxide. cc.	Equivalent metal. Mgs.	Nitrous oxide. cc.	Equivalent metal. Mgs.	Metal found. Mgs.	Metal dissolved. Mgs.	Per cent. metal found.
		Volume.	Sp. gr.													
1	65	65	1.05	6.45	0	0	6.45	10.73	58.5	248.73	2.61	29.54	289.09	300	96.36
2	60	65	1.05	6.31	0	0	6.31	10.5	59.6	253.0	2.31	26.14	289.6	..	96.54
3	65	60	1.10	16.02	0	0	16.02	26.6	54.3	230.5	3.36	38.02	295.5	..	98.5
4	60	60	1.10	23.4	0	0	23.4	33.3	52.26	221.1	4.03	45.6	300.0	..	100.0
5	25	50	1.15	34.15	0	0	34.15	56.7	51.57	218.6	1.35	15.27	290.7	..	96.9
6	20	50	1.15	40.4	0	0	40.4	67.2	52.2	221.6	1.08	10.8	286.8	..	96.2
7	20	40	1.20	60.49	0	0	60.49	100.7	45.9	194.9	295.6	..	98.5
8	20	30	1.25	74.16	68.5	0	0	74.16	123.6	39.0	165.6	289.0	..	96.3
9	20	15	1.30	173.27	204.9	76.7	52.74	111.4	235.56	285.3	..	96.1
10	20	15	1.30	176.94	203.5	64.4	44.2	150.3	250.2	294.4	..	98.1
11	17	10	1.35	177.6	251.1	177.9	122.43	104.03	173.2	295.63	..	98.54
12	17	10	1.35	177.9	261.6	202.7	139.4	94.15	156.7	296.1	..	98.7
13	0	9	1.40	186.2	320.4	340.5	234.18	40.0	66.59	300.77	..	100.25
14	15	9	1.40	178.63	314.9	329.9	226.9	42.3	70.4	297.3	..	99.09
15	50	9	1.40	180.2	315.7	327.9	225.5	44.7	74.41	299.9	..	99.9

II.—Reduction of Nitric Acid by Lead.

The results as given in Table II, were obtained from work with acids of specific gravity 1.05 to 1.35. Experiments made with stronger acids were not successful, since the insolubility of lead nitrate in strong nitric acid prevented the solution of the metal, because of the protective coating of salt formed about the latter. It will be observed that, while the reduction-products are the same as in the parallel work with copper, there is a striking difference in the relative amounts of the oxides of nitrogen produced. Thus, while the nitrous oxide equivalent of copper with 1.10 per cent. acid is only 13–15 per cent. of the metal, with lead it is as high as 62 per cent. The difference in the results obtained with the more dilute acids is even greater, and reference to the curves will show that the same contrast in the reducing power of lead and copper is found throughout the whole work. As experiments have not been made to determine the effect of temperature upon the composition of the products of reduction of *dilute* nitric acid by copper, it cannot be asserted that *all* of the observed differences in the results of the reactions with copper and lead are due to differences in the strength of metallic properties. Judging, however, from the results of experiments 1, 2, and 3, Table I, it is probable that the effect of varying temperature, for any degree of concentration of the acid, is but slight. That lead is a much more pronounced metal than copper, and that, therefore, the observed differences are to be expected, is clear from the thermo chemical investigations of Thomsen.¹ That investigation gives the number of heat units evolved in the formation of nitrates in aqueous solution [according to the formula (R,O,QAq)] for copper and lead respectively, as 52,910 and 68,070, and also the number of units evolved in the action of gaseous hydrogen acids on water-free oxides, as follows :

CuO , and $\text{PbO} + 2\text{HCl}$; 38,830 and 56,830 ;

CuO , and $\text{PbO} + 2\text{HBr}$; 46,900 and 65,630 ;

CuO , and $\text{PbO} + \text{H}_2\text{S}$; 33,750 and 49,830,

¹ Thermochemische Untersuchungen, III., 514 and 518.

II. ACTION OF LEAD ON NITRIC ACID.

Experiment. No.	Temperature.	Acid.		Winkler tube. Mgs. N_2O_3 .	Nitrometer. Mgs. N_2O_3 .	Nitrogen dioxide. Mgs.	Equivalent metal. Mgs.	Nitrogen trioxide. Mgs.	Equivalent metal. Mgs.	Nitric oxide. cc.	Equivalent metal. Mgs.	Nitrous oxide. cc.	Equivalent metal. Mgs.	Total metal found. Mgs.	Metal dissolved. Mgs. 1000	Per cent. found.
		Volume.	Sp. Gr. *													
1	95°	65	1.05	17.07	0	0	17.07	92.75	12.99	180.16	19.04	704.2	977.16	1000	97.71
2	95°	65	1.05	10.99	0	0	10.99	59.81	15.49	214.88	18.9	699.06	973.75	"	97.37
3	"	60	1.10	29.96	0	0	29.96	162.5	11.6	161.1	16.8	621.4	945.07	"	94.50
4	"	55	1.15	18.97	0	0	18.97	162.5	30.3	420.3	13.01	481.2	1004.3	"	100.4
5	"	50	1.20	20.4	0	0	20.4	110.93	31.6	438.3	10.9	403.17	952.4	"	95.24
6	"	40	1.25	24.28	0	0	24.28	132.14	39.94	583.51	8.15	301.43	987.08	"	98.70
7	"	20	1.30	27.69	28.49	0	0	27.69	150.62	45.88	635.77	4.39	162.36	948.7	"	94.87
8	"	25	1.35	78.17	103.08	55.43	124.5	57.26	311.6	24.4	338.5	4.31	166.5	941.1	"	94.11

In regard to the immediate source of nitrous oxide in reactions such as those we are considering, several explanations have been offered. Divers¹ has shown that hyponitrous acid decomposes readily into nitrous oxide and water and V. Meyer² has proven that hydroxylamine and nitrous acid react in a similar manner. Divers has also demonstrated³ that in the preparation of hydroxylamine by the action of tin on nitric acid, a much better yield is obtained if a second acid (such as sulphuric or hydrochloric) is present. I am not aware, however, that any work has been done to determine the respective quantities of nitrous oxide obtained from the solution of equal weights of metal in nitric, and in a mixture of nitric and sulphuric acids. Accordingly, near the close of the present work, I made a determination with one gram of lead, employing as a solvent, 65 cc. of nitric acid (specific gravity 1.05), and 2 cc. of concentrated sulphuric acid. The action, of course, was greatly retarded by the coating of lead sulphate on the surface of the foil so that at the close of four hours only 888 milligrams of metal, had dissolved; yet an analysis of the gases and a calculation to one gram of lead showed a yield of only 12.27 cc. of nitrous oxide, which represented a deficiency as compared with the parallel experiments (Table II, 1 and 2) of about 33 per cent. However, as the volume of nitric oxide collected was also low, no definite conclusion can be drawn from this fact. It is my intention to repeat these experiments while examining the resulting solution for hydroxylamine sulphate, with a view of determining definitely whether the source of nitrous oxide in this reaction is not to be found in the decomposition of hydroxylamine.

Conclusions.

1. Nitric acid of specific gravity of 1.30 or greater, when reduced by copper, yields only nitrogen trioxide and dioxide, the former increasing and the latter diminishing rapidly with increasing dilution of the acid.

2. Nitric oxide is a product of decomposition of nitrogen trioxide and dioxide, when the specific gravity of the nitric

¹ Proc. Lond. Roy. Soc., **19**, 425.

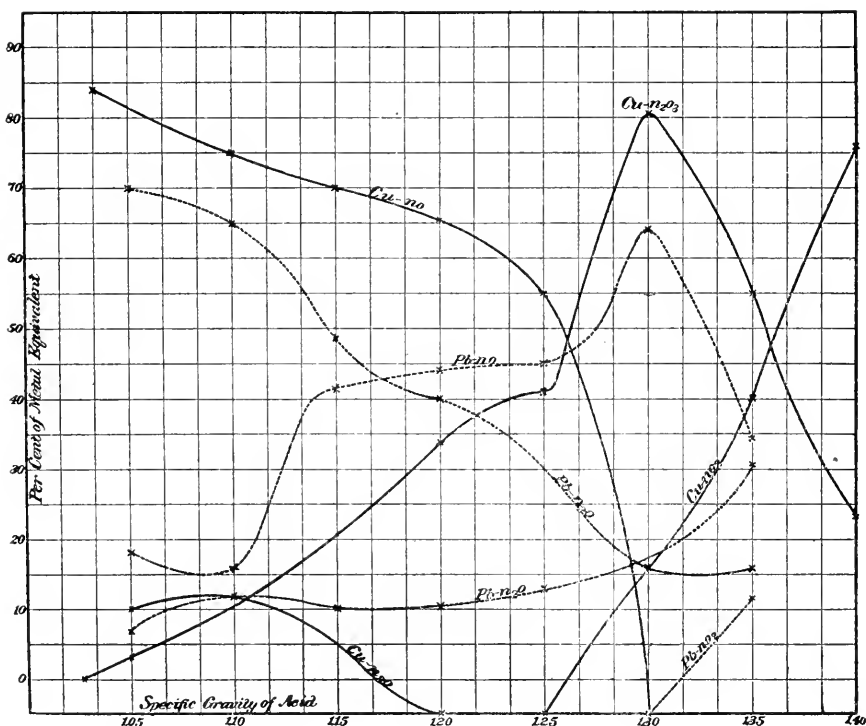
² Ann. Chem. (Liebig), **175**, 141.

³ J. Chem. Soc., **43**, 455.

acid employed is 1.25 or more; if the acid has a specific gravity below 1.25, then the trioxide only is the source of nitric oxide.

3. Lead reacts much more readily than copper, producing, with equal concentration of acid, relatively much more nitrous oxide and less of the higher oxides of nitrogen.

4. While not desiring to generalize on a too slender basis of experimental evidence, it seems to me that the remarkable difference in the composition of the products of reduction of nitric acid by lead and copper, respectively, favors the direct deoxidation theory, rather than the one which presupposes the presence of nascent hydrogen.



ANN ARBOR, July, 1894.

III. AN INTRODUCTORY STUDY OF THE INFLUENCE OF THE SUBSTITUTION OF HALOGENS IN ACIDS, UPON THE RATE AND LIMIT OF ESTERIFICATION.

BY D. M. LICHTY.

The classic work on esterification, by Berthelot and Péan de Saint-Gille,¹ and particularly the study by Menschutkin,² of the influence of the isomerism of alcohols on the rapidity and limit of esterification, suggested the use of the same process for determining the influence which substitution of halogens in fatty acids has upon the rate and the limit of their esterification. The study was begun with ordinary alcohol and monochloroacetic acid. No material was used whose purity was not first assured. The investigation was carried out by heating one or more series of mixtures of equivalent weights of alcohol and an acid. These mixtures were sealed in small tubes. The quantity of alcohol used for each trial was as nearly 0.250 gram as could be readily weighed; the capacity of the tubes was about 7.5 cc., and all were as nearly of the same size as they could be conveniently made.³ To prevent any esterification before heating, the following method was employed:

The alcohol was enclosed in sealed, thin-walled bulbs, small enough to be placed into the tubes to be used, then the theoretical quantity of acid was added, and the whole sealed. Immediately before placing into the thermostat any of these small vessels (a series of six or eight of which were heated at one time), the bulbs were broken by a quick shake. The thermostat consisted of an oil-bath, which was kept at a temperature of 154° C. by means of a Lothar-Meyer furnace⁴ and a Reichardt gas-regulator. To stop the process of esterification, or at least to reduce it to a minimum after a tube was taken from the bath, it was at once plunged, at first into tepid and then into cold water.

¹ Ann. Chim. Phys., [3], 1862, **65**, 385; **66**, 5; 1863, **68**, 225.

² Ann. Chim. Phys., [5], 1880, **20**, 287.

³ Berthelot and Péan de Saint-Gille: Ann. Chim. Phys., [3], **66**, p. 53 et seq.

⁴ Ber. d. chem. Ges., **16**, 1090, Fig. 4.

It was first deemed necessary to discover whether any of the acids, in question, acted upon glass; but neither monochloroacetic nor dichloroacetic acid had any appreciable effect. No trials were made with the other acids.

For the purpose of determining the amount of acid left uncombined at the end of a trial, I intended to use a standardized solution of barium hydroxide, following Berthelot and Menschutkin; but the first trial proved that the monochloroacetic ester is rapidly saponified by this reagent,¹ and further investigation showed that the esters of the other acids are affected in the same way, and, as would be expected, sodium, potassium, and calcium hydroxides produce the same result. Experiment developed the fact, however, that ammonia does not readily saponify, for it was shown that the weight of an acid found by titrating by means of this reagent, using a mixture of an acid and its ethyl ester, differed only by a few tenths of a milligram from the weight actually taken. Magnesia was also used to determine the amount of free acid in two series of esterifications of monochloroacetic acid. The results of these trials are given in the following tables:

Duration of esterification.	1 hour.	2 hours.	4 hours.	6 hours.	
Series I.	67.98	72.04	65.70	69.34	per cent. esterified.
Series II.	67.46	71.02	69.74	65.21	“ “
Duration of esterification.	8 hours.	10 hours.	12 hours.	54 hours.	
Series I.	68.61	67.31	34.78	per cent. esterified.
Series II.	65.82	67.79	67.09	46.93	“ “

The figures beneath the number of hours during which a tube and its contents had been heated, represent the per cent. of the acid which was esterified, *i. e.*, at the end of the first hour in Series I, 67.98 per cent. of the monochloroacetic acid was esterified, while at the end of the same interval in Series II, 67.46 per cent. of the acid was esterified, and so on.

The results with ammonia as the titrating reagent were as follows:

Duration of esterification.	1 hour.	2 hours.	4 hours.	6 hours.	8 hours.	54 hours.
Per cent. esterified.	67.01	66.78	66.91	66.61	65.81	45.58

¹The use of barium hydroxide as a means of determining the amount of unchanged acid, has possibly led to some error in the work of Berthelot and Menschutkin, although it is probable that the esters of non-substituted acids are much less rapidly saponified than are those under consideration.

The ammonia method for determining the free acid was finally definitely adopted for it was found to be much less liable to error than the one in which magnesia was used, the latter yielding no concordant results with known weights of acid while the former did. As it was discovered that water very slowly saponifies the esters, the contents of each tube after the heating, were dissolved in alcohol before titrating for free acid. The results obtained with magnesia are given mainly to show that the low per cent. of esterification attained at the end of 54 hours was not due to experimental error. No gaseous products were formed and no explanation for the low figures can now be offered, although they are undoubtedly due to some decomposition.

The per cent. of acid esterified at the end of the first hour or the "initial rate of esterification" is 67.01, while this is also the highest per cent. reached, and, therefore, the limit. The average of the first five trials is 66.62, the mean limit of esterification. The initial rate for acetic acid and ordinary alcohol is 46.95,¹ while the limit, which is reached in about 24 hours, is 66.57.

Esterification of Dichloroacetic Acid.

Duration.	1 hour.	2 hours.	4 hours.	6 hours.	8 hours.	10 hours.
Series I.	69.32	69.98	69.42	70.93	69.99	71.39
Series II.	71.00	71.26	71.20	70.97	70.83	70.44

Here again the initial rate and the limit are practically the same, the average of all the results being 70.65, that of the first series 70.24, and of the second 70.95. The average initial rate is 70.16.

Esterification of Trichloroacetic Acid.

No satisfactory results were obtained with this acid, because secondary changes, causing the evolution of gas, took place. Owing to the explosion of the tubes while being heated, only one determination of free acid was secured, the result showing that about 6.5 per cent. of the acid remained uncombined, or that 93-94 per cent. of the acid was neutralized. The presence of gas as a product of the reaction, makes it extremely doubtful whether these figures indicate the true amount of

¹ Menschutkin: Ber. d. chem. Ges., **11**, 1507 b; Ann. Chim. Phys., [5], **20**, p. 305.

acid which was esterified, as the hydrochloric acid evolved would assist in the dehydration.

Comparison of Results.

	Initial rate.	Limit.
Acetic acid	46.95	66.57
Monochloracetic acid	67.01	66.62 (average of 5)
Dichloracetic acid	70.16	70.65 (average of 12)

The limit for acetic acid is reached in about 24 hours, while that for the mono- and the dichloracetic is reached, as will be seen below, even in half an hour. The initial rate increases with the increase in the amount of chlorine. The limits for acetic acid and monochloracetic are nearly equal, while that for dichloracetic acid is about four units higher. It will also be seen that the difference between the initial rates for acetic acid and that for monochloracetic is about 20 units, and, between the initial rate for monochloracetic acid and that for dichloracetic, three units. The influence of chlorine is then by no means proportional to the number of atoms of that element, which are contained in the molecule.

In the three 54-hour determinations with monochloracetic acid, which gave lower results than those which were obtained at the end of one hour, no gaseous products were detected. No explanation can be offered for the results obtained until a more careful examination of the products be made.

One trial with each of the two chloracetic acids in which the reaction continued for a half-hour only gave the following results :

Monochloracetic acid	68.04
Dichloracetic acid	71.14

These results are higher than are those of the average limit already given.

Esterification of Monobromacetic Acid.

Duration.	$\frac{1}{2}$ hour.	1 hour.	4 hours.	8 hours.
Series I.	65.87	62.67	50.82	43.46

This series shows a rapid decrease in the per cent. of acid esterified with increase in the duration, a decrease which begins to show itself after a shorter period than in the case of monochloracetic acid and is much more marked than for the

latter acid. No gaseous products were noticed in this connection. The amount of acid esterified at the end of one-half hour is a little over two units less than in the case of monochloracetic acid.

It is very evident that the rate of esterification is remarkably accelerated by the substitution of halogens for hydrogen in acetic acid, and that in the case of the two monohalogen acids studied, a secondary reaction sets in early and causes an increase in the quantity of free acid.

I hope to conduct this investigation under more favorable conditions as to temperature, if possible, and to make the intervals, especially at the beginning, much shorter so as to make it possible to follow the course of the reactions more completely. The research will also be extended to other series of halogen substituted acids, besides those from acetic acid, with the hope of obtaining a large number of data from which to determine the influence of the position as well as of the number of substituting halogen atoms upon the rate of esterification. The especial and new problem to be attacked is, however, to ascertain the *true* initial velocity in these cases, by selecting lower temperatures than those adopted by previous investigators, and by also beginning the determination at the *shortest possible* interval after immersing the mixture of acid and alcohol in the thermostat.

ANN ARBOR, June, 1894.

IV. ON THE ACTION OF SODIUM ON THE ESTERS OF ACONITIC AND CITRIC ACIDS. PRELIMINARY NOTICE.

BY PAUL C. FREER.

If perfectly pure triethyl aconitate is dissolved in ten times its own volume of ether and the calculated quantity (one molecule) of sodium, in the form of finest wire, is then added, reaction sets in at once; the sodium becomes covered with a yellow solid, while hydrogen is evolved, the ether at the same time assuming a deep red color. If the sodium is kept clean by means of a stirrer, it gradually disappears, while the above-mentioned precipitate takes its place. A substance, having

the same composition, is also produced if sodium ethylate, in calculated quantity, is added to an ethereal solution of triethyl aconitate. In the latter reaction a deep red color is at first observed. After a few minutes the liquid becomes turbid, and finally a yellow-colored precipitate is deposited which, however,—differing from the one produced by the direct action of sodium,—is deliquescent. This sodium derivative has not the simple formula which would result from the replacing of one hydrogen atom in a molecule of the ester by means of the metal, for analysis shows that it contains 16.2 per cent. of sodium¹ (calculated for $C_{22}H_{28}O_{11}Na_4 = 16.48$ per cent. ; or for the sodium derivative of two molecules of triethyl aconitate less one of ethyl alcohol). If either of these sodium derivatives is acidified with dilute sulphuric acid, and the resulting brown solution is extracted repeatedly with ether, a thick oil is deposited upon evaporation of the solvent. The following means of purification were adopted: The oil was dissolved in dilute ammonia, a little insoluble residue filtered out, and the filtrate thereupon precipitated with lead acetate; after the excess of ammonia had been expelled, the resulting lead compound, which was nearly white, was decomposed by means of hydrogen sulphide and then filtered, while the filtrate was repeatedly extracted with pure ether. When the latter was distilled off, a clear, slightly yellow syrup remained, which did not crystallize, even after standing for some days. This syrup reacts readily with phenylhydrazine, forming a non-crystallizable compound; it imparts a deep red color to a solution of ferric chloride, and is undoubtedly a ketone. It is readily saponified by means of alcoholic potash, and a crystalline body, melting at 114° – 115° with the formula $C_9H_{12}O_5$, can be isolated after acidifying. The sodium acting on triethyl aconitate, therefore, at first replaces a portion of the hydrogen, while, subsequently, sodium ethylate separates, so that the resulting compound is a ketone.

A similar result is observed when sodium (two atoms) is added to triethyl citrate (one molecule). The hydrogen contained in the hydroxyl group is at first vigorously attacked, but subsequently the excess of metal reacts with the sodium

¹ A second sodium derivative which is soluble in ether, is also produced.

derivative so formed, separating sodium ethylate, and producing the metallic derivative of a ketone, which contains 16.5 per cent. of sodium, and is, in appearance, like that obtained from triethyl aconitate. The above experiments have also been extended to tetraethyl citrate, triethyl aconitate, and to triethyl carballylate with similar results.

Recently Dieckmann¹ inaugurated some experiments on the action of sodium on tiglic and pimelic acids, obtaining in the first case, by separation of sodium ethylate, a derivative of ketopentamethylene, and, in the second, a similar one of hexamethylene. As the work which I had begun with the ethereal salts of tribasic acids seemed to enter upon the territory taken by Dieckmann with the dibasic ones, I temporarily gave up the work. Personal information recently received by me from Dr. Dieckmann, has left this entire field to me, so that I intend once more to take up the work where I left it.

Miss N. E. Goldthwaite has executed the experimental work which has so far been done in this investigation, and I wish to take this opportunity of most heartily thanking her for her assistance.

October, 1894.

THE COMBINATION OF SULPHUR WITH IODINE.

BY C. E. LINEBARGER.

I.

INTRODUCTION.

Historical.—In the first paper ever published on the properties and reactions of iodine, it is stated that the elements, sulphur and iodine, enter into combination,² nothing being said, however, of the nature and properties of the compound.

Gay-Lussac, in his classical monograph on iodine³ writes that iodine forms with sulphur only a weak combination, which is blackish gray and indistinctly crystalline; no defi-

¹ Ber. d. chem. Ges., **27**, 102, 965.

² "Le soufre s'unit à l'iode, mais avec moins d'énergie que le phosphore."—B. Courtois: Découverte d'une substance nouvelle dans le Vareck. (Cette découverte a été annoncée le 6 décembre, à la séance de la première classe de l'Institut par M. Clément). Annales de Chimie et de Physique, **88**, p. 308, 1813.

³ Recherches sur l'iode: Annales de Chimie et de Physique, **91**, p. 22, 1814.

nite compound of the two metalloids, however, is described; indeed, Gay-Lussac regarded the two elements as being so similar in their properties and behavior, that some doubt might be placed in the possibility of their entering into true chemical combination.

Soon after the discovery of iodine, physicians and pharmacists began to look into the medicinal properties of the element and its compounds. Henry, in the *séance* of the 15th of May, 1827, of the *Société de Pharmacie*¹ communicated a process of preparing an "iodide of sulphur," for medicinal purposes, by melting the two elements together in certain proportions; these proportions, it may be stated, were afterwards changed.

Heinrich Rose² subjected to sublimation an "iodide of sulphur" made by melting iodine and sulphur together—in what proportions, he does not state. Two experiments were performed, in one of which 88.76 per cent. of iodine was found in the sublimate, while in the other, the per cent. of iodine was 92.56. Rose concludes that no definite compound of the two elements is formed in this way.

For nearly thirty years no further work on this subject seems to have been done. At the beginning of the "sixties," however, several papers appeared almost simultaneously by Rath,³ Lamers,⁴ and Guthrie.⁵

Rath's work consists in a crystallographic examination of some samples of a "hexaiodide of sulphur" prepared by Lamers in the following way: Solutions of sulphur and iodine of various proportions in carbon bisulphide were allowed to evaporate slowly at low temperatures, whereby crystals, containing six atoms of iodine to one atom of sulphur, invariably separated out, no matter what the relative proportions of the two elements in the solution had been, unless indeed, one of

¹Journal de Chimie Medicale, de Pharmacie et de Toxicologie, redigé par les Membres de la Société de Chimie Medicale, **3**, 313, 1827.

²Ueber die Verbindungen des Schwefels mit dem Chlor, Brom, und Jod: Poggen-dorff's Annalen, **27**, 115, 1833.

³Krystallographische Beiträge, 10; Dreifach Jodschwefel, SI_3 . Poggendorff's Annalen, **110**, 117, 1860.

⁴Notiz über Jodschwefel; Journal für praktische Chemie, **84**, 349, 1861.

⁵On the Bisulphide of Iodine; Quarterly Journal of the Chemical Society, **14**, 57, 1862.

the metalloids was present in considerable excess, when, before the crystallization of the hexaiodide, the element in excess separated out to some extent first. Rath was inclined to call the crystals examined by him, mere isomorphous mixtures, but hesitated to draw such a conclusion, inasmuch as he regarded sulphur and iodine to be too dissimilar elements to form isomorphous mixtures.

Lamers states that he repeated Grosourdi's experiment,¹ which consisted in passing a current of hydrogen sulphide into an aqueous solution of trichloride of iodine, and thus obtained a reddish-brown amorphous mass having a composition corresponding approximately to the formula S_3I_2 .

In Wurtz's Dictionaire de Chimie, under the head of Iodides of Sulphur, it is stated that E. Henry² has described the product of the reaction of one atom of sulphur on two of iodine, which possesses a lamellar structure and a feeble odor of iodine.

Guthrie (*loc. cit.*) investigated the reaction between sulphur chloride and the iodides of some alcoholic radicals, the product being an "iodide of sulphur in the form of fine tabular crystals of the luster of iodine." An analysis of the compound showed the simplest assignable formula to be SI .

About a year later, Sestini³ took up the investigation of melting-points and composition of mixtures of iodine and sulphur, in order to see if there really exists a compound of the two elements in definite proportions. He came to the conclusion that the two elements actually enter into combination forming a number of definite compounds instead of a mere mixture; these compounds are, he writes, in every respect analogous to metallic alloys.

Schlagdenhauffen's⁴ paper on the "Iodides of Sulphur" is an important contribution to our knowledge of the subject, although it seems never to have been duly quoted. The

¹In the dictionaries and text-books of chemistry, the reference to Grosourdi's paper is Jour. de Chim. Medicale, 9, 429. I have hunted in vain in that journal for the paper, and think that some error, clerical or otherwise, has been committed.

²Jour. de Pharm., 13, 403.

³Sur la combinaison chimique du soufre et de l'iode: Repertoire de Chimie appliquée, 5, 481, 1863.

⁴Sur l'Iodure de Soufre: L'Union Pharmaceutique, 104, 1874.

writer first determined the points of fusion of a number of mixtures of sulphur and iodine, although not with very great accuracy. He also carried out some experiments on the sublimation of previously fused mixtures of the two elements, with results similar to those obtained by Rose (*loc. cit.*). On repeating Lamers' experiments (*loc. cit.*) he found it possible to prepare a large number of compounds having the same crystallographic structure and very similar properties to Lamers' "hexaiodide of sulphur." His words in this connection are worth repeating: "When solutions of iodine and of sulphur in carbon bisulphide are mixed, a colored solution is obtained no matter what the relative quantities of the two metalloids be; no heat is evolved, hence no reaction, no combination; it is nothing but a simple mixture of the metalloids." The experiments of Guthrie were corroborated and similar ones performed. The conclusions arrived at by him are: There exists a great number of compounds of sulphur and iodine, obtainable through fusion and solution, all being of the character of alloys.

The heat of combination and of solution in carbon bisulphide, of a compound of sulphur and iodine, which is stated to have the formula S_2I_2 and "the characters of a definite body," has been determined by Ogier,¹ who found the first to be quite too small to be taken into account, and the second equal to the sum of the heats of solution of the two elements alone in carbon bisulphide.

In order to render complete the historical account of the combination of sulphur with iodine, it is necessary to mention the papers of Hautefeuille² and of Menke,³ in which certain reactions are treated of, which were supposed to yield compounds of the two metalloids, although these were not isolated and examined.

If we consider the papers which have just received brief mention, we feel that the evidence for or against the existence of compounds of iodine and sulphur, according to definite

¹ Sur les chlorures, bromures et iodures de soufre: Comptes rend., 92, 922, 1881.

² Action de l'acide iodhydrique sur quelques chlorures et sulfures: Bulletin de la Société Chimique, (2), 7, 198, 1867.

³ Reactions of Iodine and of Potassium Iodide with Sulphurous Acid: Chemical News, 39, 19, 1879.

proportions, is of an unsatisfactory nature. That iodine combines chemically with sulphur, seems probable, inasmuch as it is claimed that heat is evolved when the two elements are melted together. Still the act of solution is sometimes accompanied by the liberation of heat, and we may have to do only with a case of solution. It results from the investigations by Schlagdenhauffen (*loc. cit.*) that the two metalloids do not always crystallize out of solution in the proportions given by Lamers (*loc. cit.*). Furthermore, the reaction studied by Guthrie (*loc. cit.*) does not prove that an iodide of sulphur is actually formed, since it is quite possible that the sulphur and iodine are merely set free and crystallize as isomorphous mixtures rather than definite chemical compounds.

Object and Division of Paper.—In order to clear up, as well as possible, the doubts and obscurity about the subject of the combining of iodine and sulphur, I have taken up its investigation, repeating the old, and carrying out new experiments. Within recent years new theoretical and experimental means of deciding such questions have been introduced into science, by the judicious use of which a fair measure of success seems assured.

The division of the paper is as follows. In three sections I shall treat of the combination of the two elements: In the first, by fusion, in the second, in solution, and in the third, by double decomposition. Each of the sections is preceded by a somewhat detailed historical account of work already done, all necessary data being reproduced. This is followed either by a sketch of a theory which throws some light upon the subject, or by experimental work of my own. Then comes naturally the discussion of the results and the conclusions to be drawn from them. In the last section is given a brief *résumé* of the conclusions arrived at.

II.

COMBINATION BY FUSION OF ELEMENTS.

Historical.—Courtois (*loc. cit.*), Gay-Lussac (*loc. cit.*), and others obtained by melting together sulphur and iodine in certain proportions, a brilliant dark gray mass of crystalline structure, fusible at about 60° ., insoluble in water, by which

it is decomposed as well as by distillation. Henry (*loc cit.*), who was, I believe, the first to introduce into medicine a fused mixture of the two elements as a definite compound, recommended the taking of eight parts of iodine to one part of sulphur. Later, however, pharmacists prepared the medicament with half the above proportion of iodine. In the *Pharmacopie Raisonnée (ou Traité de Pharmacie pratique et théorique* : N. E. Henry and G. Guibourt, 3rd edition, 1841) it is stated by the authors that "they prepared it formerly with double the amount of iodine, which, being in excess, was easily liberated through heat, and was lost continually by evaporation; the proportions now adopted constitutes a chemical species more stable in its composition, but which still gives out all the time a strong odor of iodine." This pharmaceutical preparation was incorporated in the French Codex, and afterwards in all pharmacopœias, wherein may be found a full description of its mode of preparation and properties.

Sestini (*loc. cit.*) in seeking an answer to the question as to whether the pharmaceutical preparation is really a true chemical combination of sulphur and iodine, conducted a couple of series of experiments with mixtures of the two elements. In the first series he heated a mixture of known composition on a water-bath. Just as soon as the mass commenced to melt, the temperature was read off on a thermometer inserted in the mass itself, and the whole was agitated while the temperature rose slowly. Then, after it had been left in repose for several minutes, the liquid portion was poured off from the solid portion, and each was analyzed. Four such experiments were performed, the melting-points being 65.5° to 66° for the four mixtures made up of two parts of sulphur to eight parts of iodine, that is, one atom of each element. The solid portion contained from 27 to 31 per cent. of sulphur, and the liquid portion from 10 to 11 per cent. of the same element. In the second series of experiments the mixture of iodine was completely, or almost completely, melted, and then allowed to cool very slowly. The composition was then determined of a mass of crystalline structure found in the upper part of the tube in which the melting had taken place, and of another mass of lamellar structure found in the lower part of the tube.

From the results obtained, Sestini believed he could conclude that chemical combination took place, the compounds formed having a composition varying with the composition of the mixture from which they were deposited.

Schlagdenhauffen (*loc. cit.*) determined the melting-point of eleven mixtures of iodine and sulphur of varying concentrations, but his data are not accurate enough to be of much value. He himself interprets his results in such a way as to be able to make the assertion that a whole series of compounds of the two metalloids is capable of existence, characterized by having melting-points lower than those of sulphur and iodine, and losing their iodine when exposed to air.

The above somewhat detailed account of the experiments and conclusions deduced from them by Sestini and Schlagdenhauffen has been given for the purpose of exposing with sufficient fullness the way in which deductions from experimental data on this subject have been made. It is apparent that they are far from being satisfactory. This is due, in a large measure, to the fact that these investigators were guided in their researches by no good theory, if, indeed, they had any at all. In the following section a sketch is given of a theory¹ intimately applying to our subject, which may be said to possess a good basis and may be used with confidence. As the experimental data by Sestini and Schlagdenhauffen are not numerous or exact enough to permit of an application of the theory a number of experiments have been made to get additional data, of which there will be mention later on (see p. 41).

Theoretical.—The above-mentioned theory enables us, from a knowledge of the temperature at which fusion of two substances takes place and the composition of the solid phase, or, in other words, from a knowledge of the solubility of one substance in another at various temperatures—to draw pretty certain conclusions as to whether chemical combination has taken place or not. Briefly stated, the theory is as follows:

When any portion of a liquid phase of matter consisting of two substances solidifies, three cases may be distinguished:

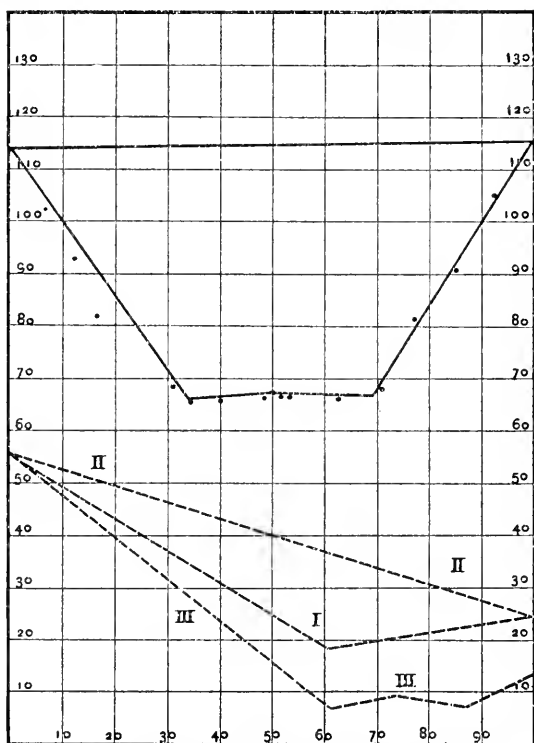
I. The two substances solidify independently.

¹ Mainly due to Le Chatelier.

II. The two substances solidify together forming isomorphous mixtures.

III. The two substances unite to form definite compounds.

These cases may be thrown into a graphical form through curves having for axis of abscissae the number of molecules (atoms) of one component contained in 100 molecules (atoms) of the mixture, and for axis of ordinates the temperatures at which fusion takes place. In Fig. 1 are drawn in dotted lines the curves characteristic of the three cases; curve I corresponding to case I; curve II to case II; and curve III to case III.



Ordinates are melting-points: Abscissae are atoms S in 100 atoms of mixture.

FIG. 1.

In the first case, the curve consists essentially of two branches cutting each other at a sharp angle, each of the branches cor-

responding to the exclusive crystallization of one of the substances. At the point of intersection of the two curves, the two substances separate out in the solid state in the same proportion as they are present in the solution, and the temperature remains constant during the change from the liquid to the solid state.

The curve representing the second case being, as it is, a straight line connecting the points of fusion of each of the component substances is quite ideal, very few, if any, mixtures presenting such a *normal* behavior; it is rare that two substances can be found which unite in all proportions to form perfectly homogeneous mixed crystals. Generally the curve is more or less convex towards the axis of abscissae, indicating non-homogeneity in the deposit, and hence a lowering of the point of solidification.

In case III we have to do with three definite chemical substances,—if the original substances combine in more than one proportion, more than three substances are formed and must be accounted for; for the sake of simplicity, we will assume that but one combination takes place—and it is seen that the curve is made up of four branches, each outside couple corresponding to case I. Should the compound formed be isomorphous with one of its constituents, the corresponding branches would have to be changed accordingly.

Experimental.—In order to determine to which kind of the theoretical curves, the curve drawn from data of mixtures of sulphur and iodine, and their melting-points belong, and thus to get an answer to the question whether chemical combination takes place between the two elements, experiments on the melting-points of mixtures of the two elements have been carried out, it being needless to say that such experiments are also determinations of solubility.

There are serious difficulties to be met with in the determination of the melting-points of mixtures of iodine and sulphur. At the temperature of fusion, iodine vaporizes rapidly and condenses in the cooler portion of the containing vessel; the composition of the melt is thus quite appreciably changed, and in addition, the vapors of iodine render the performance of an experiment very disagreeable. Attempts were made to

get satisfactory results with an apparatus similar to the one described by Küster,¹ but in vain. Finally the following method was adopted, which is simply the one now universally adopted for the determination of the melting-points of organic substances in the laboratory.

Mixtures of sulphur and iodine in various proportions were sealed up in small glass tubes, which were then heated in a bath of sulphuric acid to about 130° , and their melted contents well shaken together so as to form a homogeneous mixture. The tubes were then placed in a vertical position in the bath, which was allowed to cool down slowly. The lower half of the tubes, which alone was filled with the melt, was broken off, and coarsely powdered samples introduced into narrow thin glass tubes, such as used for determining points of fusion. A little above the substance these tubes were melted together so as to form a closed chamber and thus prevent the escape of iodine through volatilization. The glass tubes from which the samples had been taken, was dropped, mouth downwards, into a test-tube about half filled with a dilute solution of potassium hydrate, to absorb any escaping iodine. Generally, a bubble of air separated the solution from the solid melt, so that absorption took place slowly.

To determine the composition of the melts, the little tube, together with the caustic potash solution, was poured out into an evaporating dish, the test-tube rinsed out with a little water and the dish heated until the solid mixture melted and could be dislodged from the small tube. The action of the dissolved alkali was allowed to proceed for a couple of days at ordinary temperatures, the melt being crushed with a glass or agate pestle, so that all iodide could be absorbed. The sulphur was then filtered off into a Gooch crucible, dried at 100° – 105° and weighed. The iodine was determined either gravimetrically as silver iodide or volumetrically by Volhard's method.

The temperature of fusion of the substance enclosed in the thin tubes was determined in the usual way, a thermometer divided in fifths of a degree, being used. Ordinarily, three

¹ Ueber die Erstarrungspunkte isomorpher Gemische. *Zeitschrift physikal. Chemie*, 8, 578, 1891.

such tubes were prepared; with the first, the temperature was allowed to rise rapidly, and the melting-point was only approximately determined; the two subsequent determinations were made with great care. The crystals being black and yielding an opaque melt, the temperature at which fusion began was determined by watching attentively a reflecting face of a crystal, and noting as point of incipient fusion the temperature at the moment the crystal became dim; duplicate experiments gave almost identical results. The sharpness of the phenomenon of fusion varied with the proportion of the metalloids in the mixture; the degree of accuracy in the determinations may be put at less than 0.3° when the composition varied between $S=30$ to 70 , and less than 3° in the intervals $S=0$ to 30 and $S=70$ to 100 . As it is in the inner interval that the decisive data are obtained, the above degree of accuracy may be reckoned sufficient.

The sulphur used in the experiments was bought as chemically pure, but, to make sure, it was crystallized a couple of times from carbon bisulphide; its melting-point was 115° . The iodine had been sublimed twice; its point of fusion was 114.1° .

The results of the determinations are given in Table I, and are represented graphically in Fig. 1 by the full-line curve. In the table, the first column gives the number of the experiment, the second the number of atoms of sulphur contained in 100 atoms of the mixture, and the third the temperature at which fusion occurs. Data marked with a star are due to Sestini (*loc. cit.*).

TABLE I.

1. No. of experiment.	2. No. atoms S in 100 atoms of mixture.	3. Tempera- ture of fusion.	1. No. of experiment.	2. No. atoms S in 100 atoms of mixture.	3. Tempera- ture of fusion.
1.	0.00	114.1	10.	50.00	66.2
2.	6.38	102.0	11.	51.10	66.2
3.	12.14	92.0	12.	54.51	66.0
4.	14.53	83.0	13.	63.13	66.1
5.	*21.10	75.0	14.	69.72	67.6
6.	*31.03	67.5	15.	76.33	81.0
7.	34.22	65.3	16.	84.14	88.0
8.	41.09	66.0	17.	94.21	107.0
9.	48.92	66.1	18.	100.00	115.0

Discussion of Results.—The curve from the foregoing data is entirely similar to the theoretical one, No. III. We are, therefore, justified, if the theory be correct, in admitting that the two elements have entered into true chemical combination, forming a compound containing equal numbers of atoms of both elements; furthermore, only one compound can be said to exist.

It may be worth while to consider the phenomena attendant upon the addition of sulphur to melted iodine. Suppose to melted iodine just at its point of fusion, a little sulphur be added; it enters into combination with the iodine; the sulphur iodide thus formed dissolves, and in accordance with the law that fixed dissolved substances, lower the melting-point; the system can remain in a state of fusion at a lower temperature than can the pure iodine. Let more sulphur be now added; the result is that more sulphur iodide is formed, and the point of solidification is still further lowered. Let this operation be repeated until there is more iodine in a state of combination than in a state of freedom. If now, the temperature be lowered until a solid separates out, it is quite as likely that this will be the sulphur iodide as pure iodine, that is, the system may be regarded as a solution of iodine in sulphur iodide, since it is customary to regard as solvent that component of the mixture which separates out in the operation in question. In this case the addition of more sulphur, inasmuch as it increases the amount of sulphur iodide, which is now the solvent, renders the solution more dilute; the amount of free iodine increasing continually, the melting-point of the solution rises, until, after sufficient sulphur has been added to combine with all the iodine, a compound according to definite chemical proportions remains in a state of purity.

Entirely similar phenomena would be observed, if, starting with pure melted sulphur, we should add portions of iodine. Also, it may be added that no great complication would be introduced in the above considerations, if several compounds of the two elements should be formed; it would simply be necessary to treat each of the compounds or elements with the next lower or higher compound, or element, just as in the case considered above.

III.

COMBINATION IN SOLUTIONS OF ELEMENTS.

Historical.—As mentioned on page 35, Lamers (*loc. cit.*) claims to have found that from solutions of sulphur and iodine in carbon bisulphide, a compound having a composition corresponding to the formula SI_6 crystallizes out; the solutions prepared by him had the following compositions (the amount of carbon bisulphide is not given):

I.	4 equivalents of sulphur to 1 equivalent of iodine.
II.	2 " " 1 " "
III.	1 equivalent " 1 " "
IV.	1 " " 3 equivalents "
V.	1 " " 5 " "

Analyses of the crystalline deposits gave these results:

Crystals from solution.	I.	II.	III.	IV.	V.
I.	96.2	95.6	95.8	95.9	96.3
S.	3.8	4.4	4.2	4.1	3.7
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.0	100.0	100.0	100.0	100.0

Although the proportions of the two metalloids in the solution vary considerably the composition of the crystals is approximately the same, and corresponds to a compound containing six times as many atoms of iodine as of sulphur, which requires 96 per cent. iodine, and 4 per cent. sulphur.

In order to obtain this "sulphur hexaiodide," Lamers states that it was necessary to conduct the evaporation very slowly at low temperatures; if the evaporation took place rapidly at higher temperatures (summer heat), crystals containing less sulphur were obtained.

It seems contrary to our received notions that such slight changes of outward conditions should have such a considerable influence upon the composition of the product. It is doubtful whether much confidence can be placed in Lamers' observations. Rath found the specimens of the "hexaiodide" submitted to him for crystallographic examination to be more of the nature of isomorphous mixtures than well-defined compounds. As a matter of fact, we find in Schlagdenhauffen's paper statements to the effect that Lamers' "hexaiodide" is not the only compound formed in solutions of sulphur and

iodine in carbon bisulphide, but that it is merely a "member of the same family of compounds which are all soluble after their fusion in carbon bisulphide." Schlagdenhauffen does not, however, communicate any numerical results, contenting himself with general statements. No other work seems to have been done on this phase of our subject, if we except the thermo-chemical investigation by Ogier (*loc. cit.*).

Experiments on the Crystallization of Carbon Bisulphide Solutions of Iodine and Sulphur.—To get data that may aid in judging of the value of Lamers' and Schlagdenhauffen's observations, I have carried out some experiments on the crystallization of the two elements from carbon bisulphide solution. Concentrated solutions containing the metalloids in the proportion of one atom of sulphur to one atom of iodine were allowed to evaporate very slowly at temperatures varying from 10° to 15° . In a little over 24 hours, crystals began to separate out around the sides of the crystallizing dish at the point of juncture of the liquid and the glass, some samples of which were removed and analyzed,¹ a composition corresponding to the formula $S_n I_n$ (n being any whole number) being found. In a day or so, new crystals which had been deposited were taken and analyzed, identical results being obtained. And, finally, when all the solvent had evaporated, some crystals in the bottom of the dish were found to have the same composition. It seems evident then that under these circumstances, a compound of iodine and sulphur is formed containing an equal number of molecules of each of the elements. How Lamers obtained the results given in his paper from solutions of the same concentration as the one which I examined it is impossible to say, especially since he lays such emphasis upon the conditions according to which the crystallization must take place, and apparently worked with considerable care. In this connection it may be added that his experiments and observations on the influence of a change of temperature upon the product obtained also seem to need revision. So far as Lamers' work is concerned, it is very probable that his "hexaiodide of sulphur" is not a definite chemical compound, although it can not be with certainty affirmed that such a combination of atoms is incapable of existence.

¹ The analysis was carried out in the same way as described for melts of the two elements on page 42.

Experiments on the Changes of the Boiling-Point of Carbon Bisulphide Caused by the Addition of Iodine and Sulphur.—If to a solution of sulphur in carbon bisulphide, iodine be added, the latter will bring about practically the same lowering of the vapor tension or raising of the boiling-point as it would, were the sulphur not present, provided that no combination between the two metalloids take place. If, however, combination occurs, the lowering of the vapor tension or the raising of the boiling-point will be less in the proportion that the iodine has combined with the sulphur. Here, then, we have a means of judging whether chemical union takes place between the two elements in solution.

A number of determinations on the raising of the points of ebullition of solutions of iodine and sulphur in carbon bisulphide have been made with a view of getting some exact data on the subject; the apparatus employed was the well-known Beckmann's ebullioscope, with the modifications recommended by Linebarger.¹ As a necessary preliminary to such determinations, the elevation of the boiling-points of solutions of iodine and of sulphur alone must be determined. Happily, such determinations have been very carefully made by Beckmann² for iodine and sulphur, and by Helff.³ For convenience of reference their results are reproduced here in abridged form in Tables II and III.

TABLE II.

Beckmann's Experiments with Iodine.

No. of experiment.	Grams iodine in 100 grams CS ₂ .	Boiling-point elevation.	Molecular mass of iodine.
1.	1.268	0.120°	251
2.	2.910	0.270	256
3.	2.964	0.265	266
4.	6.03	0.521	275
5.	6.08	0.550	263
6.	8.97	0.777	274
7.	12.98	283

¹ Some Modifications of Beckmann's Ebullioscopic Apparatus. Chem. News, 69, 279, 1894.

² Ueber die Molekulargrösse des Jods, Phosphors und Schwefels in Lösungen. Zeitschrift physikal. Chemie, 5, 76, 1890.

³ Molekulargewichtsbestimmungen der Verbindungen von Phosphor mit Schwefel und Schmelzpunkte von Gemengen beider Elemente. Zeitschrift physikal. Chemie, 12, 196, 1893.

TABLE III.

Beckmann's and Helff's Experiments with Sulphur.

No. of experiment.	Grams sulphur in 100 grams CS ₂ .	Boiling-point elevation.	Molecular mass of sulphur.	Name of experimenter. (B, Beckmann; H, Helff.)
1.	1.17	0.107°	259	H
2.	1.572	0.151	247	B
3.	2.72	0.243	265	H
4.	2.895	0.276	249	B
5.	3.153	0.294	255	B
6.	4.033	0.355	270	B
7.	5.24	0.455	273	H
8.	6.14	0.540	270	B
9.	5.98	0.516	275	B
10.	7.70	0.655	279	H
11.	9.04	0.770	279	B
12.	9.32	0.761	290	H
13.	12.08	0.985	294	H
14.	14.09	1.083	308	H
15.	15.13	1.210	297	B
16.	16.23	1.264	304	H
17.	21.00	1.590	314	B
18.	22.00	1.597	326	H
19.	27.82	1.920	343	H

These tables show that there is an ever-increasing complexity in the molecules of both sulphur and iodine as the concentration becomes greater. In the case of iodine, values of the molecular masses give an average of about 254, which corresponds to the molecular formula I₂. In the case of sulphur, however, it is apparent that, while in the most dilute solutions the molecular mass is about 256, corresponding to the formula S₈, in the most concentrated solutions, the molecular mass has increased to about 320, and the molecular formula must be S₁₀. This changeability in the size of the molecule introduces considerable confusion, yet it may be possible to get some light upon the subject under investigation. In the following table are given the results of my determinations on the boiling-points of solutions of mixtures of iodine and sulphur in carbon bisulphide.

TABLE IV.

*Iodine and Sulphur in Carbon Bisulphide.*MOLECULAR ELEVATION FOR 100 GRAMS $\text{CS}_2 = 23.7^\circ$.

Grams of solvent.	Grams substance.	Elevation of boiling-point.	Parts substance in 100 parts solvent.	Molecular masses.
32.03	1.1641	0.348°	3.64	248

IODINE CALCULATED IN CASE OF COMBINATION.

32.03	2.7240	0.778°	8.51	260
"	4.4043	1.214	13.75	269
"	7.4890	1.943	23.41	286
"	10.2123	2.449	31.90	309
"	11.6520	2.793	36.41	313
"	12.4516	2.940	38.90	315

CALCULATED FOR IODINE.

32.03	1.5600	0.430°	4.87	273
"	3.2402	0.866	10.12	277
"	6.3249	1.594	19.76	293
"	9.0482	2.151	28.27	310
"	10.2875	2.460	33.08	318

The molecular masses calculated in either way are without any essential difference. If we assume that the molecule of sulphur in moderately concentrated solutions, is made up of eight atoms ($\text{S}_8 = 256$), and that of iodine in the same conditions consists of two atoms ($\text{I}_2 = 254$) it is seen that the values of the molecular masses in the last table correspond well to those in the two preceding ones; and as the concentration increases, the molecular masses become greater. This behavior may be interpreted in two ways: either there is no combination and the increase in molecular size is to be attributed to an ever-increasing complexity in the molecules of the elements, or there is a partial combination of the two metalloids which augments with the concentration.¹ It is not easy to decide which of these two proposed interpretations is the more correct; indeed, it is probable that increase of size in the molecules of the elements, as well as chemical combination, take place at the same time. A circumstance which warns us not to draw conclusions except with the greatest

¹ The molecular mass of a compound represented by the formula S_2I_2 is 318, a number identical with that experimentally found in the most concentrated solutions.

circumspection, is that, in concentrated solutions, the ebullioscopic method is not entirely reliable.

We may, by other experimental means, get some light upon the subject of the chemical combination of sulphur and iodine dissolved in carbon bisulphide. In case of combination, heat changes must occur when solutions of the two metalloids are mixed; and in this connection the thermo-chemical research by Ogier (*loc. cit.*) may be discussed, and better cannot be done than to quote his own words: "*Iodure de soufre*.—L'iodure de soufre solide S_2I " (in atomic notation S_2I_2) "est formé à partir des éléments avec un effet thermique très sensiblement nul, ainsi qu'il résulte des expériences suivantes. D'une part, j'ai mélangé des solutions d'iode et de soufre dans le sulfure de carbone, et je n'ai observé aucun dégagement de chaleur. D'autre part, la dissolution du produit tout formé.



Or ce nombre est précisément égal à la somme des chaleurs de dissolution de l'iode et du soufre dans le sulfure de carbone, Le composé avait d'ailleurs les caractères d'un corps défini, il serait donc formé avec un dégagement de chaleur très voisin de zéro....."

Ogier does not indicate the concentrations of the solutions of sulphur and iodine which he mixed, so that from his statements only the conclusion that in dilute solutions there is no combination between the two elements is legitimate. It would be important to make some experiments on stronger solutions to see if the same conclusion holds good for them also. Unhappily no thermo-chemical apparatus is at my disposal.

If a compound of sulphur and iodine is formed in the solution, it is evident that its molecular mass is in the vicinity of 300 to 320. Now the molecular mass of a compound corresponding to the formula S_2I_2 is 318; it is, perhaps, justifiable to take this formula which from its analogy to the formula of sulphur chloride S_2Cl_2 might almost be expected, as the formula of the possibly formed compound of the two elements. As a compound corresponding to this formula was found to

be the only one obtainable by simultaneous fusion of the two elementary substances, it is probable that it is the only one formed in solution also. It can not be admitted that molecules of the formula SI were present in the solution in any considerable amount, the molecular mass of such a compound being too small; nor is it possible that a "hexaiodide of sulphur" was formed, as its molecular mass is too large; in either case, the ebullioscope furnishes sufficiently accurate indications as to its impossibility.

IV.

COMBINATION BY DOUBLE DECOMPOSITION.

Historical.—Guthrie (*loc. cit.*) states that when sulphur chloride and ethyl iodide are mixed together at ordinary temperatures, no heat is evolved, nor is there any other evidence that chemical action takes place. After sealing up in a glass tube one molecule of sulphur chloride and a little more than one molecule of ethyl iodide, and allowing the mixture to stand for twelve hours, he found on opening the tube that ethyl chloride escaped, and "magnificent" crystals were deposited, the analysis of which showed them to contain one atom of sulphur to one atom of iodine. Guthrie remarks that methyl and amyl iodides are susceptible of similar reactions, but "for obvious reasons the ethyl compound is preferred."

Schlagdenhauffen (*loc. cit.*), in continuation of Guthrie's work, studied the action of some inorganic iodides upon the sulphur chlorides, finding that if the iodide of ammonium and of potassium were sealed up with some sulphur chloride in the proportions necessary for the production of the sulphur iodide described by Guthrie, and, if the mixture be heated on a water-bath, the liquid rapidly assumes a dark violet color, due to the formation of sulphur iodide which stays in solution. After the mixture has been heated for several hours the decomposition is complete, and by repeated washings with carbon bisulphide, the chloride of ammonium and of potassium can be obtained white and pure, while through evaporation of the carbon-bisulphide solution, a crystalline

residue remains, melting at 92° to $94^{\circ 1}$. The iodide of mercury and of lead also yield the sulphur iodide when heated to the temperature of boiling water in sealed tubes with sulphur chloride. In studying the reaction of iodoform on sulphur chloride, Schlagdenhauffen ascertained that the sulphur iodide was also obtained.

In the experiments mentioned in the preceding lines, no particular examination of the product of the reaction seems to have been made. Guthrie, it is true, analyzed it, but is it not possible that the analyzed substance was merely an isomorphous mixture of the two elements in proportions which happened to be atomic? Is it not plausible that the products of the reaction are ethyl chloride, together with sulphur and iodine in a state of freedom and not in combination? From the nature of the reaction and the proportions of the reacting substances, it is necessary that the two elements be in about the same proportions, whether they are free or combined. Schlagdenhauffen paid but little attention to the product obtained in the double decompositions effected by him, and the melting-point which he gives, 92° to 94° , seems to indicate that the product, if it be S_2I_2 , which has a melting-point 66.2° , is quite impure.

Experimental.—I have carried out a number of experiments on the reactions between sulphur chloride and some organic iodides in order to gain more precise knowledge of the nature of the reaction and its product. The mode of operation was the following: A large test-tube of rather thicker glass than the ordinary was heated in a blowpipe flame at about a third of its length up from the closed end, and drawn out into a slender tube three to four inches long. Another constriction was made in the middle of the open part of the tube. When a mixture of an organic iodide and of sulphur chloride is poured into such a tube it occupies the lower chamber, and the tube is sealed at the upper constriction. After the reaction has taken place, and crystals have separated out from the liquid,

¹ Schlagdenhauffen gives as melting-points of the sulphur and iodine used by him 107° and 112° , respectively. This seems to indicate that he worked with quite impure material; hence, the observations and results obtained by him may have a certain qualitative value, but as quantitative data but little reliance can be placed in them.

the tube is inverted so that the mother-liquor may drain off from the solid mass without its being necessary to open the tube; in this way all action of the air and its moisture is avoided.

Reaction between Sulphur Chloride and Ethyl Iodide.—A mixture of one molecule of sulphur chloride¹ with considerably more than one molecule of ethyl iodide² was filled into three tubes of the same size and shape as described above, and sealed. One of the tubes was placed where it was exposed to direct sunlight for three to four hours a day, while the other two were covered with black paper and set in a dark closet. For the sake of brevity let us designate the first tube by A, the second by B, and the third by C.

On the second day of exposure, the solution in A had turned reddish brown, and an abundant crop of crystals had separated out. The tube was inverted so that the mother-liquor could drain off; two kinds of crystals were distinguishable in the mass,—slender needles seemingly transparent, and black, ill-defined, rhombic tablets.

The contents of B and C showed no change save a very slight darkening in color after standing for three days in darkness. The tube B was then heated to 99° while exposed to diffuse daylight, for half an hour. The liquid turned black and, after standing over night in a dark closet, a fine crop of crystals was deposited, in which were distinguishable two forms similar to those found in A, although here the interlaced, needle-like, transparent crystals were present in greater number. The contents of the tube C, which were carefully shielded from light, and were kept at a temperature of 15° to 20°, gradually turned darker and darker, but no separation of crystals took place until after about two weeks; in this case also, two kinds of crystals were present.

These experiments show that, as might, indeed, be expected, light and heat exercise considerable influence upon the velocity of the reaction, but not so much on the nature

¹ The sulphur chloride had been purified by repeated rectification; its boiling-point was 137.9° under 758 mm. pressure.

² The ethyl iodide had been fractionally distilled until a considerable quantity, boiling constantly at 72.2° under a pressure of 756 mm., was obtained. This was preserved from the decomposing action of light in a dark closet.

of the product. Additional experiments were carried out with varying proportions of the reacting liquids and under different conditions of temperature and illumination, from which it appears that raising the temperature and intensifying the illumination hastens the reaction, which in all cases yielded two sorts of crystals, although their relative quantity varied somewhat.

Samples of these crystals were subjected to analysis. The transparent ones contained almost pure sulphur, while the black ones contained iodine and sulphur in equal atomic proportions, that is, they consisted of a sulphur iodide corresponding to the formula S_nI_n . The cause or causes of the appearance of two kinds of crystals must be sought in the different solubilities of sulphur and iodine in the menstruum. In the first part of the reaction, the liquid is supersaturated with both the elements, which combine in crystallizing out to form the iodide, just as certain salts crystallize out of solution with formation of double salts. This necessitates the admission that the sulphur iodide is, to a certain degree, dissociated in solution; and the experiments on the combination of the two elements in carbon-bisulphide solution renders this admission justifiable. As soon as the solution through the deposit of the compound begins to approach saturation, or, in other words, ceases to be supersaturated with respect to the compound, iodine, owing to its greater solubility, tends to remain in solution, while the sulphur separates out alone. It was often observed that mother-liquors deposited on evaporation relatively large quantities of sulphur, a fact in corroboration of the explanation of the phenomenon proposed above. There is here an interesting and undoubtedly fruitful field for crystallographic research, many peculiarities in the modes of crystallization and forms of crystals due to the mutual influence of the three substances being observed. This is especially the case in the crystalline products obtained by the action of sulphur chloride on propyl iodide, to be described in the following paragraph.

Reaction between Sulphur Chloride and Propyl Iodide.—52 grams of normal propyl iodide¹ and 20 grams of sulphur

¹ The propyl iodide had been repeatedly fractionally distilled, and only a portion boiling at 102.5° under a pressure of 759 mm. was taken.

chloride were sealed up in a tube similar to that described on page 52, and the whole was exposed to diffuse daylight for about fourteen of the twenty-four hours. The color of the mixture darkened gradually, and on the fourth day a magnificent crop of homogeneous crystals had separated out; these had the form of rhombic tablets, often of great regularity and beauty. No sulphur crystals were present. The tube was turned upside down so as to let the mother-liquor drain off, and then that part of the tube containing the crystalline mass was sealed off. The mother-liquor, after standing for some days, deposited an additional crop of crystals, as a yellow mass (sulphur), in which were imbedded several comparatively large and well-formed octahedra. This indicates that the solubility of sulphur and iodine in this menstruum is more nearly equal than in a mixture of ethyl iodide and chloride, together with sulphur chloride. This experiment was repeated with slightly varying proportions of the reacting liquids. The results were always about the same; in one case some sulphur crystals were found in the first crop of crystals. An analysis of some of the rhombic crystals gave the accompanying results:

	Found.	Calc. for S_2I_2 .
Sulphur	20.22	20.12
Iodine	79.78	79.88
	<hr/> 100.00	<hr/> 100.00

Some determinations of the molecular mass of this product in carbon bisulphide solution were made by the ebullioscopic method, the results of which are communicated on page 56, *et. seq.*

Reaction between Sulphur Chloride and Amyl Iodide.—Four grams of sulphur chloride and 10.90 grams of amyl chloride¹ were sealed up in a tube with two constrictions and set in a dark closet. In five days crystals of two sorts had separated out long yellow bars of sulphur and dark rhombs (S_2I_2 ?). No further experiments were made with the amyl halogen compound, as the product obtained was too heterogeneous for utilization. The difference of solubility of the two elements

¹ The amyl chloride was a product found in the collection of the laboratory, and was considerably colored by free iodine; no attempts were made to purify it beyond a single distillation.

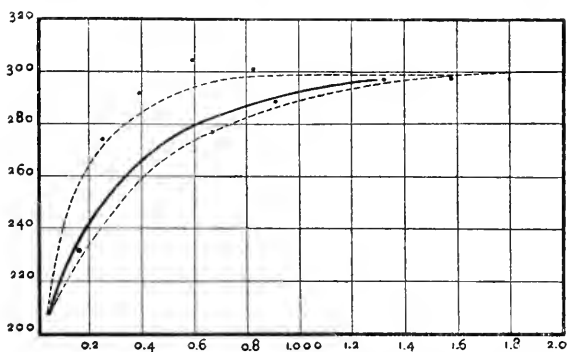
in this menstruum is more marked than in the two previous cases.

Molecular Mass of the Product of the Reaction of Sulphur Chloride on Propyl Iodide.—The same apparatus was used as for the experiments recorded on page 49, and carbon bisulphide was the solvent. The results of the determinations are given in Table V, and are represented graphically in Fig. II.

TABLE V.

Molecular Mass of S_nI_n in Carbon-Bisulphide Solution.

a		
GRAMS $CS_2 = 32$.		BAR = 759 MM.
t	m	M
Raising of boiling-point.	Grams substance in 100 grams CS_2 .	Molecular mass.
0.040°	0.35	208
0.312	3.84	288
0.860	10.25	283
1.727	21.32	293
b		
GRAMS $CS_2 = 38$.		BAR = 760 MM.
t	m	M
0.277°	3.28	281
0.485	6.13	299
0.770	9.66	297
c		
GRAMS $CS_2 = 32$.		BAR = 757 MM.
t	m	M
0.040°	0.35	207
0.640	7.48	277
1.442	18.00	295



Ordinates are molecular masses. Abscissae are temperature-elevations.

FIG. 2.

The data are platted in a system of co-ordinates, of which

the axis of abscissae represent elevations of boiling-points and the axis of ordinates, molecular masses. The dotted curves represent the results of the first and third series of determinations given in the table, while the heavy full line curve is intended to be a mean of both. The curves resemble completely the so-called dissociation curves; as the dilution increases, the molecular mass decreases, as might be expected from the experiments communicated on page 49. Let us consider what takes place when the sulphur iodide is dissolved in carbon bisulphide, making the assumption that in very dilute solution it is completely dissociated into its elements. The experiments of Beckmann (*loc. cit.*) and Helff (*loc. cit.*) show that the curve representing the connection between the molecular mass of iodine and sulphur and temperature elevation in solution are dissociation curves. Iodine has a molecular mass in mean equal to 254, and corresponding to the formula I_2 , and sulphur may be said to have, in moderately concentrated solutions, a molecular mass equal to 256, corresponding to the formula S_8 . In very dilute solution it is probable that these molecular complexes break up into simpler ones and even into the atoms. We see that in these last experiments the maximum molecular mass is a little short of 300; and it is probable that it would in more concentrated solution increase somewhat, perhaps to 318. It may be concluded here as on page 50 that the molecular formula of the sulphur iodide is S_2I_2 , but that in solution it is more or less dissociated. There seems to be more affinity between the sulphur and the iodine atoms to form complex elementary molecules than to enter into combination with each other; the sulphur iodide is much of the nature of a double salt of the class referred to in my paper, "On the Existence of Double Salts in Solution."¹

Crystalline Product Obtained from Solution of S_2I_2 in Carbon Bisulphide.—A solution of sulphur iodide (S_2I_2) which had been prepared in a molecular mass determination was poured into a crystallizing dish, covered with an inverted larger dish, and allowed to stand at temperatures varying from 15° to 20° . In a short time crystals separated out along the edges, some

¹ This Journal, 15, 337-347, 1893.

of which were removed and analyzed. The results of the analysis were :

	Found.	Cal. for S_2I_2 .
Sulphur	20.83	20.12
Iodine	79.17	79.88
	<hr/>	<hr/>
	100.00	100.00

The solution was allowed to stand until all the solvent had evaporated, leaving a crystalline residue in the bottom of the dish. Some of these crystals were picked out, and their analysis gave the accompanying results :

	Found.	Calc. for S_2I_2 .
Sulphur	20.17	20.12
Iodine	79.83	79.88
	<hr/>	<hr/>
	100.00	100.00

These experiments show that, if it be admitted that the compound of sulphur and iodine is dissociated into molecular aggregations of the elements when in solution, combination supervenes during the act of crystallization.

V.

CONCLUSIONS.

The conclusions to be drawn from what precedes are evident. Experiments on the fusion of mixtures of iodine and sulphur, on their behavior when dissolved in carbon bisulphide, and on double decompositions of their compounds indicate that but one definite chemical compound is formed. It cannot be said, however, that other compounds of the two elements are incapable of existence ; only, the above detailed experiments give no indications of their formation. The compound formed contains equal numbers of atoms of sulphur and iodine, and its molecular formula is S_2I_2 . Experiments on the boiling-point of its carbon bisulphide solutions, as well as the analogy with the chloride and bromide of sulphur (S_2Cl_2 and S_2Br_2) show this to be without doubt correct. The melting-point of the product from fusion of elements as well as that from double decomposition, was approximately the same ; *viz.*, 66.1° to 66.2° . No special crystallographic examination was

made of the products obtained in the various ways mentioned above, but all seemed to assume more or less pronouncedly the form of rhombic tablets. The compound S_2I_2 is in a very weak state of combination; it partakes more of the nature of the so-called "molecular compounds" than of that of true chemical compounds; there seems to be more tendency on the part of the iodine and sulphur atoms to form molecular aggregations than to combine with each other.

Chicago, Ill., September 17, 1894.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XII. AN INVESTIGATION OF THE TWITCHELL METHOD FOR THE DETERMINATION OF ROSIN IN SOAP.

BY THOMAS EVANS AND I. E. BEACH.

When Twitchell published his method for the determination of rosin it was hoped by many that a sure means of accomplishing the desired result had been obtained. Unfortunately this was not fully justified by later experiments. Lewkowitch has shown¹ that Twitchell's process gives fairly good results, especially when the volumetric method is used, but that, while it is undoubtedly the most satisfactory process known, it is far from being exact. As Twitchell's method will be frequently referred to, a sketch of the process taken from the original article² is here given.

The gravimetric method is carried out as follows: Two or three grams of the mixture of fatty acids and rosin are dissolved in ten times their volume of absolute alcohol in a flask, and dry hydrochloric acid gas is passed through in a moderate stream. The flask is placed in a vessel of water to keep it cool. The hydrochloric acid is rapidly absorbed and, in about 45 minutes, the ethers separate and float upon the surface of the solution and no more hydrochloric acid is absorbed. The flask is removed from the bath and allowed to stand a half-hour longer to insure a complete combination of the alcohol and fatty acid. It is then diluted with about five

¹ J. Soc. Chem. Ind., **20**, 1893.

² J. Anal. Appl. Chem., **5**, 379.

times its volume of water, and boiled until the acid solution is clear, the ethers with the rosin in solution floating on top. To this some naphtha is added, the whole transferred to a separatory funnel, the flask being washed out with naphtha. The acid solution is thus run off and the naphtha, which should amount to about 50 cc., washed once with water and then treated with five grams of caustic potash, which has been dissolved in five cc. of alcohol and 50 cc. of water, and agitated. The rosin is immediately saponified and the two layers separate completely. The rosin soap is then run off, treated with acid, the rosin collected in any manner desired, dried, and weighed.

The volumetric method is similar to the gravimetric in its first stages, except that the contents of the flask are washed into the separatory funnel with ether instead of naphtha, and the ether solution is thoroughly washed with water until the washings are no longer acid. Fifty cc. of previously neutralized alcohol are then added to the ether and the solution titrated with standard caustic soda.

According to Lewkowitch a loss of from 10-15 per cent. of rosin occurs when the gravimetric method is used; this he endeavored to account for but was unsuccessful.

Taking up the process with a desire to render it more exact we performed various experiments upon the same general line as Twitchell's. The samples subjected to analysis were, in most cases, prepared by mixing a known weight of rosin with a known weight of a mixture of equal parts of oleic acid and the doubly pressed fatty acids used in candle making. The rosin and fatty acids were mixed in such quantities that the resulting sample weighed about 50 grams. After mixing, the beaker containing the rosin and fatty acids was heated upon the water-bath until the contents were entirely melted, when it was cooled rapidly, being continually stirred in order to avoid separation by crystallization. It was found in each case that the rosin lost no appreciable weight by this heating, while it was always necessary to make a correction for the loss of fatty acids.

In etherizing, it was found advantageous to dissolve the sample in absolute alcohol in a 100-cc. cylinder and to place

this in a large jar containing water and a little ice. In each case two samples were etherized at the same time so as to obtain parallel results when the conditions were known to be practically the same.

In carrying out the volumetric method Twitchell's directions were followed very closely, and in the gravimetric, the recommendation of Lewkowitch, to wash the petroleum-ether layer repeatedly with a large excess of dilute caustic potash, was found greatly to facilitate separation.

The results obtained by the volumetric method when use was made of the combining weight 346 (given by Twitchell), were found to be somewhat too high, and this was at first supposed to indicate incomplete etherification of the fatty acids. It was found, however, that if the alcoholic solution, saturated with hydrochloric acid gas, was allowed to stand over night before diluting with water and boiling out the alcohol upon the water-bath, the results were appreciably lower, and that an addition of sulphuric acid to the alcohol used for dissolving the samples and standing over night as before, produced a further lowering of the percentage of rosin found. Finally, the use of methyl alcohol, instead of ethyl for etherification, appeared to give exceedingly good results as may be seen from the following table:

PERCENTAGE OF ROSIN.

		Combining weight 346.		Combining weight 328.9			
		Theo- retical.	Found.	Differ- ence.	Found.	Differ- ence.	No.
According to Twitchell with ethyl alcohol.	{	40.13	42.19	+2.06	40.10	—0.03	61.
		40.13	41.74	+1.61	39.67	—0.46	76.
		40.13	42.16	+2.03	40.06	—0.07	62.
		40.13	41.69	+1.56	39.62	—0.51	63.
		40.13	41.12	+0.99	39.08	—1.05	74.
Stood 18 hours before boil- ing out with water.	{	40.13	40.31	+0.18	38.32	—1.71	54.
		40.13	40.60	+0.47	38.59	—1.54	45.
		40.13	40.77	+0.64	38.76	—1.27	52.
		40.03	39.88	—0.15	37.92	—2.11	48.
Two cc. H ₂ SO ₄ added to alcohol; stood 41 hours.	{	40.13	39.53	—0.60	37.58	—2.55	34.
		40.13	39.46	—0.67	37.51	—2.62	35.
Two cc. H ₂ SO ₄ added to alcohol, stood 21 hours..		40.13	40.03	—0.1	38.05	—2.08	36.
Two cc. H ₂ SO ₄ added to alcohol; stood 18 hours..		40.13	40.40	+0.27	38.41	—1.72	38.

	Combining weight 346.		Differ-	Combining weight 328.9		
	Theo-	Found.	ence.	Found.	Differ-	No.
Two cc. H_2SO_4 added to alcohol; stood 18 hours..	40.05	40.38	+0.33	38.38	-1.67	40.
Methyl alcohol; stood 1 hour	40.05	39.93	-0.12	37.96	-2.09	5.
“ “ “ $1\frac{1}{2}$ “	40.03	39.94	-0.11	37.97	-2.08	27.
“ “ “ $1\frac{1}{2}$ “	40.03	40.04	+0.01	38.06	-1.97	11.
“ “ “ $1\frac{1}{2}$ “	40.03	39.99	-0.04	38.01	-2.02	12.
“ “ “ 1 “	40.03	40.05	-0.02	38.07	-1.96	17.
Ethyl alcohol + 2 cc. H_2SO_4 ; } stood $\frac{1}{2}$ hour.	40.13	41.59	+1.46	39.53	-0.60	
	40.13	41.89	+1.76	39.82	-0.31	

Since the rosin used in these experiments was high grade, being WG and free from foreign matter, it was at first supposed that its combining weight would be about 346, the number given by Twitchell. Repeated titration proved that this was not the case and that the combining weight was 328.9—which is very much lower than anything found by either Twitchell or Lewkowitch, the lowest combining weight found by the latter being 340.8. The last two columns in the table show the percentages of rosin actually found and their differences from the theoretical.

The foregoing analyses were selected from a series of 85 and show that methyl alcohol gives poorer results than ethyl, and that standing over night before boiling out the alcohol, causes considerable loss. These large losses upon standing and upon etherization with methyl alcohol may be attributed either to a slight etherification of the rosin or to decomposition. The fact that Twitchell and, later, we were unable to isolate any ethers of rosin makes the latter theory the more probable.

Although the time required for etherification, the volume of alcohol and the presence of sulphuric acid seemed at times to affect the results, a close study of the whole series of analyses shows that their influence was very slight.

The temperature of the bath surrounding the solution undergoing etherification, had apparently no effect upon the results, provided this temperature did not rise above 20° . If the bath is allowed to become warm, or if a very rapid stream of hydrochloric acid gas is passed through the alcoholic solution, the results are considerably lowered.

The results obtained by using ethyl alcohol and boiling out

very soon after etherizing are fairly uniform and correspond approximately with the theoretical and, while generally they are better than those reported by Lewkowitch, they differ from his quite strikingly, in that they are lower than the theoretical while his, on the whole, are higher.

Several experiments were made by weighing out the fatty acids and rosin into the graduated cylinder, dissolving in alcohol, and etherizing in the usual manner. Each of these determinations was run in check with a sample prepared in the manner first described, with the following results:

	Theoretical percentage.	Found.	Difference.
Special sample	39.87	39.36	—0.51
Ordinary sample	40.13	39.67	—0.46
Special sample	38.95	38.04	—0.91
Ordinary sample	40.13	39.08	—1.05

Since the results obtained from these specially prepared samples agree so well with those from the samples prepared in the ordinary manner, it is evident that no substantial error was introduced by the method of preparing the samples.

The rosin contained in the samples referred to was the ordinary commercial article, and, since this consists largely of resin acid anhydrides, it was deemed advisable more closely to approach the conditions of a rosin determination in a soap where the rosin would probably exist as the hydrated resin acids. With this end in view a mixture of known weights of fatty acids and rosin was saponified with alcoholic potash, the alcohol expelled by evaporation, the residual soap dissolved in water and decomposed with sulphuric acid. The fatty acids and rosin so obtained were washed free from mineral acid, dried, extracted with ether, this last expelled, and the residue used as a special sample. The results obtained from samples prepared in this way agreed very well with those prepared in the usual manner.

Finally, fearing that the fatty acids used in these samples, and those contained in an ordinary rosin soap, might differ in their behavior upon etherification, and thus tend to influence the results, several portions of the mixed oleic and solid fatty acids used in our work were dissolved in alcohol and carried through the volumetric method in the usual manner.

At the same time a sample of soap stock, such as is ordinarily used in preparing rosin soap, was obtained through the kindness of a Lawrence soap manufacturer, and the fatty acids obtained from this were treated like the mixture of oleic or solid fatty acids.

The fatty acids used in preparing the samples gave :

	1.	2.	3.	4.	Average.
Percentage unetherized acid	1.58	1.91	1.42	1.44	1.59

The fatty acids from soap stock gave :

	1.	2.	3.	4.	Average.
Percentage unetherized acid		1.70	1.72	1.88	1.77

These results, added to those previously mentioned, show conclusively that the method of preparing the samples was satisfactory and could lead to no false conclusions.

Both Twitchell and Lewkowitch carried out experiments like those just mentioned. The former found 0.97 per cent. unetherized matter in the fatty acids, which he attributed to a small amount of resin contained in the original fat. Wilson¹ in repeating Twitchell's experiments found 0.7 per cent. unetherized fat, while Lewkowitch obtained 2.28 per cent. from pure (?) stearic acid, and 5.1 per cent. from pure (?) oleic acid. The last named attributed these large percentages to incomplete etherization and seemed inclined to doubt the results of both Twitchell and Wilson. Our results, while not agreeing with those of the latter chemists, certainly approach them more closely than those of Lewkowitch.

Several attempts were made to etherize rosin alone with the following results :

Wt. of Rosin.	Rosin calculated from titration.	Difference.	Percentage loss.
2.0968 gms.	2.054	0.0428	2.00
2.4723 "	2.45	0.0223	0.90
2.035 "	2.016	0.019	0.93
2.03 "	2.016	0.014	0.69
2.115 "	2.091	0.024	1.14

As was to be expected from the analysis of mixtures, a much larger loss of rosin occurred when methyl alcohol was used in place of ethyl. Two such determinations are given :

¹ J. Soc. Chem. Ind., 10, 952.

Wt. of Rosin.	Rosin calculated from titration.	Difference.	Percentage loss.
2.0116	1.865	0.1466	7.3
2.0738	1.938	0.0358	6.6

From the tabulated results it is easily seen that when the combining weight of the rosin is known, the volumetric method gives results within the limits ordinarily required in a soap analysis. The combining weight proved to be a disturbing factor and a series of determinations was made upon various commercial samples. Those in the first column were made from a sample box of the various commercial grades of rosin, while those in the second were from rosins obtained from soap manufacturers:

No.	Grade.	Combining weight.	No.	Grade.	Combining weight.
6	WW	339.9			
7	WG	344.5	1	WG	328.9
8	N	347.5	5	N	351.4
9	M	339.8	3	M	334.5
10	K	355.6			
11	I	355.9			
12	H	354.6			
13	G	354.9			
14	F	336.8	2	F	333.5
15	E	347.9			
16	D	346.9			
17	C	350.3			

From the foregoing is seen that the combining weight of rosin varies widely in both directions from that given by Twitchell, and what is still more disappointing is that the grade, which is determined largely by the color, has little or no relation to the combining weight; so that even when the grade of rosin used is known, there is no definite basis upon which to calculate the combining weight.

Since the gravimetric method gives such untrustworthy results, the only possible way out of the difficulty seemed to be to separate the rosin gravimetrically, determine its combining weight, and use the factor so obtained in the volumetric process. Lewkowitch mentions this device as being evidently of little avail, but as he did not mention any experiments it was deemed worthy of trial.

Five grams of a mixture containing forty per cent. WG rosin (combining weight 328.9) was run through the gravimetric method and the resin acids dried at 105° C., and titra-

ted. The combining weight of these acids was found to be 328.6 in one experiment and 325.8 in another.

Four experiments with rosin N (combining weight 351.4) were then tried and negated the results obtained with rosin WG, as the titrations gave the combining weights 329; 323.9; 331.1; 329.4. The cause of this difference was evidently due to one of two causes: either the rosin had been partially etherized or it contained unsaponifiable matter. In order to determine the cause of the discrepancy the gravimetric method was investigated more carefully.

Lewkowitch found that in carrying out this method as originally proposed by Twitchell, there was a small loss of rosin, due to incomplete saponification when shaking out the petroleum-ether layer with dilute caustic potash. This loss Lewkowitch found he could avoid by repeated extraction of the petroleum-ether layer with dilute caustic potash. He also found a more important loss in the acid wash-water first run off from the petroleum-ether solution of the products of etherification. This he recovered by extracting the wash-water with ordinary ether; but a still larger loss—which he found to be about 15 per cent.—Lewkowitch was unable to account for, although he gave as his opinion that part of the rosin was decomposed by the action of hydrochloric acid, forming acids of lower molecular weights and, possibly, condensation-products.

On reviewing his work there was evidently but one place to look for this loss; *viz.*, in the petroleum-ether layer from which the saponifiable rosin has been removed by caustic potash. Accordingly a sample of rosin N (combining weight 351.4) was run through the gravimetric method and the petroleum-ether layer, after repeated extraction with caustic potash and the complete separation of the resulting resinate solution, was evaporated to dryness. A gummy mass with a strong odor suggestive of turpentine, was thus obtained, which in one case equalled 9.71 and in another 9.54 per cent. of the original rosin. The percentages of rosin obtained from the alkaline extraction were found to be 86.78 and 86.06, thus making totals of 96.49 and 95.59 per cent. The loss in these experiments (0.07 and 0.08 gram, respectively) was probably due to experimental error.

In order to make sure that the matter obtained from the petroleum ether was not an ether, it was tested with alcoholic potash and found to be unsaponifiable. Several portions of N rosin (combining weight 351.4) were now dissolved in petroleum ether and extracted with caustic potash. The petroleum ether, on being evaporated off, left a residue of unsaponifiable matter which amounted to 8.8, 9.1, and 9 per cent., respectively, of the rosin employed. This residue looked and smelled exactly like that obtained when the rosin had been subjected to the action of hydrochloric acid. The slight excess of about 0.5 per cent. found when the rosin had been carried through the gravimetric process, may be due to decomposition, as it will be remembered that the volumetric method showed a loss of about one per cent. of rosin. A rosin and fatty-acid mixture prepared from WG rosin (combining weight 328.9) gave a loss of five per cent. of rosin by the gravimetric method, which corresponds exactly with the percentage of the unsaponifiable matter contained in this sample. Four other samples of rosin were tested for unsaponifiable matter with the following interesting results :

No.	Grade.	Percentage of unsaponifiable matter.	Combining weight of original rosin.	Calculated combining weight of saponifiable rosin.
6	WW	7.34	339.9	315.0
1	WG	5.00	328.9	312.4
5	N	9.00	351.4	319.7
8	N	8.21	347.5	319.0
9	M	7.61	339.8	314.0
				Average, 316.0

The fact that the combining weights of the saponifiable portion of the various samples of rosin agree so well seems to bear out the statement of Maly¹ that colophony is essentially an anhydride of abietic acid.

This subject is being investigated by one of us while the other has undertaken the task of perfecting a method for the separation of the unsaponifiable rosin from the hydrocarbon oils employed as soap-fillers, etc. When this has been accomplished the Twitchell method will leave little to be desired from the soap-analyst's point of view.

¹ Jsb., 1861, 389.

A LABORATORY METHOD FOR THE PREPARATION OF POTASSIUM FERRICYANIDE.

BY M. S. WALKER.

The usual laboratory methods for the preparation of potassium ferricyanide by the action of chlorine or bromine water upon potassium ferrocyanide are not very satisfactory because there is generally a considerable quantity of the ferricyanides of iron formed at the same time. Several methods have been devised to overcome this difficulty, but these methods give only fair results when used by most students.

With a view to overcoming the objections to the chlorine and bromine methods, as they are employed in the laboratory, the oxidation of potassium ferrocyanide with potassium permanganate was tried and the method described below has been found very satisfactory.

Dissolve 26 grams potassium ferrocyanide in about 200 cc. cold water and add 8 cc. ordinary concentrated hydrochloric acid. Into this pour slowly a cool solution of 2 grams potassium permanganate in about 300 cc. water. The oxidation is complete if a drop added to a ferric chloride solution gives a brownish-red color but no precipitate.

Neutralize excess of acid with chalk or barium carbonate, filter, and evaporate *on the water-bath*. The first crystals will be pure. The others may contain chlorides which can be separated by fractional crystallization.

By this method beautiful crystals of pure potassium ferricyanide are obtained in the first crystallization. The crystals obtained by this method show a large development of the plane $\infty P \infty$ which rarely appears in the first crop of crystals obtained by either the chlorine or bromine methods.

This method is recommended for laboratory use because it is easy to apply, and the ferricyanide obtained is pure and shows the characteristic form of crystallization.

REVIEWS.

DESCRIPTIVE INORGANIC GENERAL CHEMISTRY. A text-book for Colleges. By PAUL C. FREER, M. D., Ph. D. (Munich), Professor of General Chemistry and Director of the Laboratory of General Chemistry, University of Michigan. Revised edition. Boston: Allyn & Bacon, 1894. 550 pp. Introductory price, \$3.00.

This book is intended for those who "have some knowledge of the elementary principles of the science." To quote from the preface: "If an elementary course, in which every stated fact has been proved by actual experiment, precedes the work given in this book, the pupil will then be amply fitted to look at chemical phenomena from the basis of the atomic theory. It is in the hope that such a preparatory course has gone before, that I have begun this text-book with the atomic theory."

In arranging the material the author has, in the main, followed the periodic law, with such deviations as experience has shown to be called for in teaching. In general terms the work has been well done, and we have as a result an interesting, readable text-book of chemistry that is up to date. It is not an easy matter to exhibit much originality in the presentation of the fundamental facts and principles of chemistry. Probably there is no other branch of knowledge that has as many text-books as this, and it is fair to assume that most of those teachers of chemistry who have any power of presentation have tried their hands at making books. Let the work go on. Some time *the* text-book of chemistry will appear. Meanwhile we all learn something from the better new ones—sometimes, to be sure, we learn "how not to do it."

In dealing with matters of theory the author is conservative. Thus, speaking of the subject of valence, he says: "Chemists are apt to allow themselves to forget how far experiment has gone, and thus to confuse the theory and its application with the phenomena of nature. The terms 'valence' or 'bond,' used to express the means of union between atoms, may become to them material things; the lines used on paper to express the supposed manner of union of atoms may simulate real linking between existing atoms, so that at the present time, the science of chemistry is in danger of being discredited by a too dogmatic conception of the application of these methods." Occasionally, this caution is forgotten, as when, on page 4, he says: "If I subdivide any compound body,

water for instance, I can continue the operation until I arrive at the smallest individual particle thereof, a molecule." And a similar lack of caution is shown on page 442, where these words occur: "Indeed, were we acquainted with seven hundred elements, instead of seventy, these seven hundred would no more be unconnected individuals than are our present number. They, too, would fall into an arrangement, in periods and families, as the elements now do; only with such a large number of individuals, the change from family to family would not present such an abrupt transition as at present." This seems highly probable, to be sure, but more than this we are not justified in saying.

In most text-books of inorganic chemistry, the subject of constitution is still treated dogmatically, that is to say, not logically. Professor Freer cannot be accused of dogmatism. He weighs the reasons carefully and states his conclusions in such a way that the student can see the connection between the facts and the theory. One cannot help wishing that he had adopted the simple view, now commonly held, that the alums are derived from two molecules of sulphuric acid, as indicated in the formula $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$. This view cannot, of course, be proved to be correct, but it is in accordance with views held in regard to many other classes of compounds, and is better than that which is expressed by the formula $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$. This makes alum a "double salt" in the old sense, and the author distinctly expresses his disapprobation of the "double salt" in the old sense, on page 336.

Professor Freer has made the attempt to trace "the relative influence exerted by the masses of the atoms which go to make up the molecules." What he means by this is shown by the following quotation: "The hydrogen compounds of the elements of the nitrogen family show a chemical character which differs from that found in the other two groups which have been studied, and the reason for this difference is to be found in the greater number of hydrogen atoms which are joined to one atom of the typical element contained in them. The hydrogen compounds of the halogens are acid, because one atom of each of those elements can unite with but one atom of hydrogen; the positive character of the latter, therefore, is not sufficient to counterbalance the negative properties of the halogen. The elements of the sulphur family form hydrogen compounds which are but slightly acid; for the two hydrogen atoms contained in these have twice the effect of the one in the chlorine group, while, lastly, the hydrogen compounds of the elements of the nitrogen family are either basic or neutral, for here the three hydrogen atoms entirely counterbalance the

chemical character of that of the element with which they are united." While it must be conceded that there is something in these considerations worthy of further study, this question will suggest itself: Ought not marsh gas to be more strongly basic than ammonia, if the preponderance of hydrogen is the cause of the basic properties of the latter compound?

I. R.

AN ELEMENTARY CHEMISTRY. By GEORGE RANTOUL WHITE, A. M.,
Instructor in Chemistry at Phillips Exeter Academy. Boston: Ginn
& Co., 1894. 272 pp.

In the preface the author says that most students who take up chemistry for one, two, or three years, never intending to be chemists, waste their time. With this statement the writer of this notice is strongly inclined to agree. Mr. White has developed a somewhat novel method of approaching the study of chemistry in regard to the merits of which it is difficult to form an opinion without trying it. The first hundred pages of the book are taken up with directions for laboratory work, the character of which does not differ essentially from that given in several well-known elementary books. The chief difference between it and similar books, is seen in the lack of systematic arrangement of the subject-matter. Under Experiments, beginning page 11, after a short chapter which treats of measuring, weighing, and the wash-bottle, iron is first taken up. The pupil is directed to make certain observations on the physical properties of iron, and then to heat a weighed quantity of iron filings in a crucible, and afterwards to weigh and note the increase in weight. He is then asked: "What has caused the gain?" No answer is given in the book, and it is difficult to see what answer the pupil is to make. He can not answer without getting the necessary information either from his teacher, or some book, and this is certainly not "finding out all things for himself." Then come these words "Let us call that which has come from the air and fastened itself to the filings—oxygen, and the new dull-black substance formed—oxide of iron. Let us call oxide of iron a compound, because it is obviously compounded of two other substances. Let us call iron itself, a simple substance, because we can not make it from two or more other substances, nor can we get two or more other substances from it. What is a simple substance? What is a compound?" Can a pupil be said to have found out for himself what a compound is, and what an element is when he has performed this experiment? The second experiment involves the use of ordinary phosphorus and, in spite of the exclamation points, and the

word CAUTION three times repeated in bold-faced type, the experiment does not seem to be an appropriate one for the very beginning of a course.

The twelfth experiment is headed, "A second oxide of sulphur," and has, of course, to do with sulphur trioxide. The results of this experiment are so intangible that it can not leave a clear impression on the mind of the pupil.

Part II treats of additional experiments. These deal with bromine, iodine, fluorine, arsenic, antimony, bismuth, and the metals, tin, lead, silver, gold, platinum, and aluminum.

Part III treats of the "History and Development of the Laws and Theories of Chemistry." Experiments necessarily play a minor rôle in this part, but they are introduced wherever it seems that they will be of service. While much of that which is presented is well presented, on the whole the tone is too elevated for the beginner—at least for such beginners as have come under the observation of the writer.

I. R.

A SHORT HISTORY OF CHEMISTRY. By F. P. VENABLE, Ph. D., Professor of Chemistry in the University of North Carolina. Boston: D. C. Heath & Co., 1894. 163 pp.

The author of this little book has for some years past given his classes a short course on the history of chemistry, because from his own experience, and that of his students, he has reached the conviction, that the study of the history is one of the best aids to an intelligent comprehension of the science of chemistry. This book is based upon the course given. It is clearly written, and is interesting. One can not but admire the skill of the author that has enabled him to condense so much in so small a space, and yet to avoid squeezing the juice out of it.

I. R.



AMERICAN CHEMICAL JOURNAL.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.¹

BY WOLCOTT GIBBS, M. D., *Rumford Professor Emeritus in Harvard University.*

[Continued from p. 417, Vol. 7.]

PLATINO-TUNGSTATES.

In a notice of these and corresponding compounds of molybdenum published some years since,² and intended to be only preliminary, I pointed out the analogy between them and the silico-tungstates of Marignac. The notice in question requires correction in several particulars, and I shall here give the results of a more complete investigation, conducted with better facilities for work and with a much wider acquaintance with the whole class of complex acids.

Platinic hydrate, like silicic hydrate, dissolves when boiled with solutions of alkaline tungstates belonging to the meta-tungstic series. Platino-tungstates are formed under these circumstances, but various conditions require to be considered. In general, I have been accustomed to prepare the hydrate $\text{Pt}(\text{OH})_4$ by Frémy's method, that is, by boiling a solution of platinic chloride with a large excess of sodic hydrate for some

¹ Presented at a meeting of the American Academy of Arts and Science, held August 1, 1894.

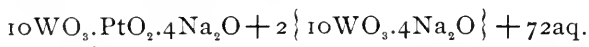
² Ber. d. chem. Ges., 10, 1384, 1877.

time and then adding acetic acid in small excess, when the platinic hydrate separates as a pale buff-yellow slimy compound to be washed by repeated decantation with cold water. When the last portions of saline matter have been removed the wash-water becomes turbid and settles only after very long standing. The hydrate obtained in this way sometimes dissolves very readily in hot solutions of alkaline tungstates, sometimes only after long boiling, and sometimes is almost insoluble. The process is therefore an uncertain one at best. The platino-tungstates formed have a yellow or orange-yellow color, and, in many cases, crystallize well. By the process which I have given, it is usually difficult to obtain perfectly saturated compounds unless a rather large excess of platinic hydrate is employed. When this is the case a greater or less quantity of a deep orange-red solution is sometimes formed, which, on standing, deposits a dark tarry mass in case the sodic tungstate is employed. In place of sodic hydrate I have also used baric hydrate in preparing a soluble form of the platinum compound, but in this case also the platinic hydrate, according to varying conditions, varied very much in solubility.

When platinic hydrate is boiled with a solution of 10:4 sodic tungstate, the latter being in large excess, yellow solutions are sometimes formed, which, on evaporation and standing, yield large crystalline masses with a fine yellow color and strong luster. These crystals consist essentially of the 10:4 sodic salt, $10\text{WO}_3 \cdot 4\text{Na}_2\text{O} + 23\text{aq.}$, but they contain a greater or less proportion of a platinic compound which—water of crystallization apart—has probably the formula



and which appears to be isomorphous with the tungstate. A compound of this kind gave on analysis figures which corresponded very closely with the formula



We may have here a combination of two isomorphous salts, having, respectively, the formulas, $10\text{WO}_3 \cdot \text{PtO}_2 \cdot 4\text{Na}_2\text{O} + 26\text{aq.}$, and $10\text{WO}_3 \cdot 4\text{Na}_2\text{O} + 23\text{aq.}$ The analyses of two different preparations of the salts correspond very closely.

The difficulty of obtaining definite compounds by direct

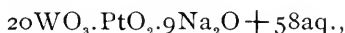
solution of platinic hydrate led me to another method, which may be used with much advantage. Pure crystallized sodic tungstate is to be dissolved in water, a rather large excess of sodic hydrate added, and a neutral, or nearly neutral solution of platinic chloride added to the boiling solution in small portions at a time. Platinic hydrate is formed and instantly dissolved. The chloride is to be added until a distinct excess of $\text{Pt}(\text{OH})_4$ is present. Acetic acid is then to be added in small excess. Alcohol then often throws down a dark tarry mass which contains one or more saturated platino tungstates. When the proportion of platinic chloride necessary, happens to be exact, a beautiful orange-colored clear solution is formed, which, on cooling or evaporation, deposits an abundance of beautiful yellow needles, or prisms, easily purified by recrystallization. By this process a definite salt may be prepared in a very short time and in large quantity. Different salts are, however, formed under different conditions, and further investigations must show whether it is possible, by using definite quantities of platinic chloride and of sodic tungstate, to obtain uniform results as regards the constitution of the salt formed. It is indispensable to employ pure platinic chloride or chlorplatينات. Even traces of iridium give a greenish tint to the platino-tungstates formed, a fact which misled me in my earlier experiments. Contrary to my preliminary statement, I now find, on more prolonged study, no isomeric platino-tungstates.

10:1:6 *Sodic Platino-tungstate*.—12:5 sodic tungstate very readily dissolves platinic hydrate in its soluble form, and gives a fine deep orange-colored solution, which, on standing, yields a mass of ill-defined dull orange crystals. These may be redissolved, recrystallized, and dried on woolen paper. Of these crystals:

1.1460 grams	gave 0.8430 gram $\text{Pt} + \text{WO}_3$	= 73.56 per cent.
1.1806 grams	gave 0.0686 gram $\text{Pt} + \text{WO}_3$	= 73.57 “
1.1806 grams	gave 0.0706 gram Pt	= 5.98 “
1.1460 grams	gave 0.8695 gram Pt	= 6.06 “
1.8770 grams	gave 0.7774 gram WO_3	= 67.83 “
0.8770 gram	lost on ignition 0.1397 gram $\text{O} + \text{H}_2\text{O}$	= 15.93 per cent.

- (2) 1.4847 grams gave 0.0466 gram Pt = 3.73 per cent. PtO₂.
- (3) 1.0976 grams gave 0.0345 gram Pt = 3.65 per cent. PtO₂.
- (5) { 1.4154 grams gave 1.0467 grams Pt = 3.83 per cent.
1.4154 grams gave 1.0129 grams WO₃ = 71.57 per cent.
- (6) 1.4847 grams gave 1.0619 grams WO₃ = 71.50 per cent.

The analyses lead to the formula



which requires:

		Calculated.	Mean.	Found.		
20WO ₃	4640	71.73	71.53	71.57	71.50	
PtO ₂	226.5	3.50	3.74	3.73	3.65	3.83
9Na ₂ O	558	8.63	8.68		8.67	
58H ₂ O	1044	16.14	16.05	16.00	16.09	
	<hr/>	<hr/>				
	6468.5	100.00				

The solution of this salt has a strongly acid reaction with litmus. It gives with ammoniac chloride beautiful colorless scaly crystals, slightly soluble in cold, but soluble in boiling water, exactly resembling in appearance the sodio-ammoniac tungstate, 12WO₃·Na₂O·4(NH₄)₂O, and containing no platinum. This reaction seems to support the view that the compound is a double salt, and we may, perhaps, assume that it is represented by the formula



The principal reactions of this salt are as follows:

With AgNO₃, a white fine grained crystalline precipitate settling slowly.

With TiNO₃, a similar precipitate in rather coarser grains.

With SO₄Cu, a very pale blue, or bluish-white fine-grained precipitate.

With HgNO₃, a bright yellow amorphous precipitate.

With Co(NH₃)₆Cl₃, a pale buff precipitate quickly becoming crystalline in leaves.

A quantity of this platino-tungstate was precipitated by a solution of mercurous nitrate. The fine yellow mercurous salt was well washed and then decomposed by dilute chlorhydric acid, the platino-tungstate being in very small excess.

The clear yellow filtrate on spontaneous evaporation deposited a pale yellow substance which may prove to be the corresponding acid.

30:2:15 *Sodic Platino-tungstate*.—This salt was obtained under the same conditions as the last, and formed granular efflorescent dull yellowish crystals readily soluble in water. Of this salt:

{ 1.3231 grams gave 0.9787 gram $\text{WO}_3 + \text{Pt} = 73.97$ per cent.
 { 1.3231 grams gave 0.0510 gram Platinum = 4.49 per cent.
 PtO_2 .

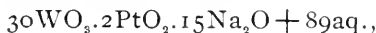
1.0144 grams gave 0.0410 gram Platinum = 4.70 per cent.
 PtO_2 .

1.5776 grams lost on ignition with WO_3Na_2 0.2657 gram
 $\text{O} + \text{H}_2\text{O} = 16.71$ per cent.

1.5776 grams gave 1.1059 grams $\text{WO}_3 = 70.06$ per cent.

1.3231 grams gave 0.9271 gram $\text{WO}_3 = 70.03$ per cent.

The analyses lead to the formula



which requires:

		Calculated.	Found.	
30 WO_3	6960	69.98	70.03	70.06
2 PtO_2	453	4.56	4.49	4.70
15 Na_2O	930	9.35	9.24	
89 H_2O	1602	16.11	16.18	
	<hr/>			
	9945			

A solution of this salt also gives white scaly crystals with potassic and ammoniac salts. It gives a white flocky precipitate with baric chloride, and a pale yellow flocky crystalline precipitate with mercurous nitrate. The compound is probably, like the last described, a double salt and may have the formula



The solution of the salt is acid to litmus. Analysis by Dr. Morris Loeb.

30:1:12 *Sodic Platino-tungstate*.—I obtained this salt by boiling platinic hydrate with 10:4 sodic tungstate for some time in a platinum vessel. It formed very large masses of

honey-yellow heavy crystals, very easily soluble in water. Of this salt:

1.1441 grams lost on gentle heating 0.1583 gram $H_2O = 13.84$ per cent.

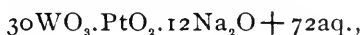
0.9383 gram lost on gentle heating 0.1313 gram $H_2O = 13.99$ per cent.

1.8069 grams gave 1.4033 grams $WO_3 + Pt = 77.66$ per cent.

0.8809 gram gave 0.6847 gram $WO_3 + Pt = 77.72$ per cent.

¹ ——— gram gave ——— gram Platinum = 2.46 per cent. PtO_2 .

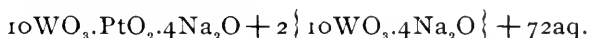
The analyses agree with the formula



which requires:

	Calculated.		Found.	
$30WO_3$	6960.0	75.44	75.53	75.43
PtO_2	226.5	2.45		2.46
$12Na_2O$	744.0	8.06		8.15
$72H_2O$	1296.0	14.05	13.84	13.99
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	9226.5	100.00		

In the analyses the water was determined by heating in an air-bath, and not by ignition. No correction for oxygen of PtO_2 is therefore applied. The solution of the salt gives the characteristic white scaly crystals with NH_4Cl and KCl , and as in the last two cases we may safely assume that the compound is a double salt. The most probable formula considering the mode of formation is



From the above it appears that, strictly speaking, none of the compounds described correspond to the silico-tungstates of Marignac, all of which appear to contain four molecules of basic oxide. Such platinum compounds may, however, exist in combination, as seems to be shown in the salts last described.

The other metals of the platinum group will probably be found to form similar compounds. Want of material has prevented a careful study of the subject, but a number of qualitative tests made with small quantities of salts of iridium, ruthenium, palladium, and osmium appeared to show clearly

¹ The data of this analysis were accidentally lost.

mium salt by precipitating its solution with mercurous nitrate and decomposing the well-washed mercurous salt by solutions of the chlorides of other metals.

4:2:2 *Platino-molybdate of Ammonium*.—The solution from which the yellow ammonium salt, first described, separated by crystallization gave, on evaporation, a dark-colored liquid over a heavy oily deep brown-red substance. This last was washed with a little ice-cold water and gradually dried to a transparent dark brown-red mass which broke up into clean sharp brilliant fragments. Of this salt:

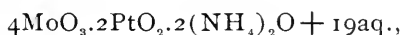
{ 0.4502 gram lost on careful heating 0.1297 gram = 28.81 per cent. $\text{H}_2\text{O} + \text{NH}_3 + \text{O}$.

{ 0.4502 gram gave 0.1226 gram Platinum = 31.63 per cent. PtO_2 .

0.5398 gram gave 0.0402 gram $(\text{NH}_4)_2\text{O} = 4.91$ per cent. NH_3 .

0.4917 gram gave 0.0369 gram $(\text{NH}_4)_2\text{O} = 4.87$ per cent. NH_3 .

The analyses lead to the formula

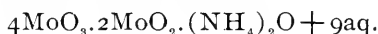


which requires:

		Calculated.	Found.
4MoO ₃	576	40.03	39.56
2PtO ₂	453	31.48	31.63
4NH ₃	68	4.72	4.91
19H ₂ O	342	23.77	23.97
	<hr/>	<hr/>	
	1439	100.00	

As in the last case the molybdic oxide is estimated by difference which in the present state of our knowledge of analysis is the most accurate method. The salt can hardly have been absolutely pure. Water decomposes it and gives an opaque buff-yellow compound which I have not examined. It will be seen from the above that the platino-molybdates described do not correspond, in general composition, with the only silico-molybdates known in which the ratio of molybdic to silicic oxide is as 12:1.

Rammelsberg¹ has described a molybdate of the dioxide and ammonium which has the formula



In endeavoring to prepare a class of stannio-tungstates I obtained a sodium salt the solution of which gave, on evaporation, a hard, nearly colorless, glassy mass. This gave, on analysis, results which did not correspond very well, but the mean of several led to the formula

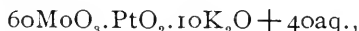


The compound deserves further study, and is not without interest in connection with the two salts noticed above.

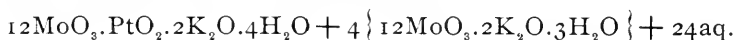
60:1:10 *Platino-molybdate of Potassium*.—This salt was obtained by boiling potassic molybdate with an excess of potassic hydrate, and adding a solution of PtCl_6H_2 until platinic hydrate which at first dissolves as fast as formed, was in small excess. Acetic acid was then added to an acid reaction. On standing, fine granular yellow crystals were formed in quantity. These were dissolved in hot water and recrystallized. Of this salt:

0.5191 gram gave 0.0098 gram Pt = 2.20 per cent. PtO_2 .
 0.5191 gram gave 0.5665 gram MoS_3 = 81.85 per cent. MoO_3 .
 0.6459 gram lost on ignition with WO_4Na_2 0.0447 gram =
 6.92 per cent. $\text{O} + \text{H}_2\text{O} = 6.61 \text{ H}_2\text{O}$.
 1.2241 grams lost on ignition with WO_4Na_2 0.0872 gram =
 7.12 per cent. $\text{O} + \text{H}_2\text{O} = 6.81 \text{ H}_2\text{O}$.

The analyses lead to the formula



which may be written provisionally as



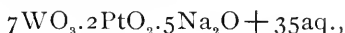
The formula requires:

		Calculated.	Found.
60 MoO_3	8640.0	82.04	81.85
PtO_2	226.5	2.16	2.20
10 K_2O	994.0	8.97	9.24
40 H_2O	720.0	6.83	6.61 6.81
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	10530.5	100.00	

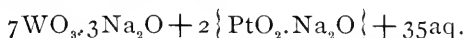
¹ Ann. der Phys., Pogg., 127, 291.

This salt is readily soluble in hot water without apparent decomposition. It gives a very pale yellow crystalline precipitate with argentic nitrate and a pale greenish-blue precipitate with cupric sulphate, which is soluble in an excess of this last.

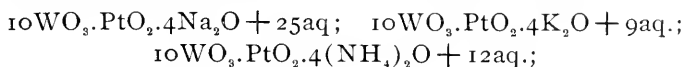
Rosenheim has recently described¹ another platino-tungstate with the empirical formula



and regards it as a double salt,



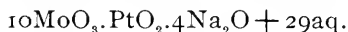
This salt was obtained by boiling normal sodic tungstate, WO_4Na_2 , in concentrated solution with platinic hydrate, and presented small yellow needles which could not be recrystallized without decomposition. He did not succeed in obtaining platino-tungstates by boiling platinic hydrate with various meta-tungstates, and suggests that the three salts which I described in my preliminary notice were mixtures of meta-tungstates (para-tungstates) and platinic oxide. They were, on the contrary, perfectly well defined and crystallized, as were also the platino-tungstates and platino-molybdates described in this paper. Further investigation will probably show that a number of other salts can be obtained by the method which I have described in which the platinic hydrate is brought in contact with acid tungstates or molybdates in the nascent state. Phospho-platino-tungstates and similar molybdenum compounds appear also to exist. A solution of 24:1:2 phospho-tungstate of sodium readily dissolves platinic hydrate on boiling, and gives an orange-colored solution which after filtration and evaporation deposits ill-defined orange crystals. When a solution of ammoniac chloride is mixed with the solution obtained as above, a beautiful orange crystalline salt is thrown down. In a preliminary notice published in 1877,² I described the preparation and properties of platino-tungstates having respectively the formulas



¹ Ber. d. chem. Ges., 24, 2397.

² Ber. d. chem. Ges., 10, 1384; Am. J. Sci., [3], 14, 61.

and of a platino-molybdate with the formula



All of these tungstate compounds were obtained by boiling



with the soluble form of platinic hydrate. The molybdenum compound was obtained in a similar manner, but I am not now able to state what acid molybdate of sodium was employed. I have not succeeded in obtaining these compounds a second time, and in the long interval of time which has elapsed since the publication of my preliminary notice the notes of description and analyses have been lost. I can only express my conviction that more extended investigations will show that no error has been made, and that the compounds unite as described. I will further remark, that, taking the analyses which I have given in this paper, it may be possible to give simpler formulas for some at least of the salts described. The formulas given, represent, I believe, most accurately the results of the analyses, but as the percentages of platinum are relatively small the quotients of these percentages by the atomic mass of platinum are very small divisors. On the other hand, the quotients obtained by dividing the percentages of tungstic or molybdic oxide by the molecular masses of tungstic or molybdic oxide are relatively very large, and the ratio between the two quotients in question becomes somewhat uncertain. The compounds which I have obtained by the method which I have given of bringing platinic oxide *in statu nascenti* into contact with the solutions of acid tungstates or molybdates gives such well-defined and beautifully crystalline salts that the subject will doubtless attract the attention of other chemists. I will make the suggestion that possibly the salts which I described in my preliminary notice may be obtained by adding ammoniac chloride to the solutions of the double salts described in this paper, so as, in the case of the tungstic compounds at least, to precipitate the tungstic oxide not combined with platinic oxide in the form of

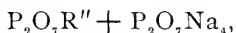


or an analogous salt. The solution should then contain only

a platino-tungstate. The application to the platino-molybdates described is less probable.

SECOND SERIES OF PYROPHOSPHO-TUNGSTATES AND PYROPHOSPHO-MOLYBDATES.

When sodic pyrophosphate is added in excess to a solution containing a metallic salt, the precipitate which is at first found is, in many cases, redissolved with formation of a double salt of sodium and the metal in question. In a certain number of cases, the heavier metal in the new compound is not replaceable under ordinary conditions, and does not exhibit characteristic reactions with tests. These facts are, of course, familiar to all chemists. Persoz supposed that these salts might be represented, in the case of divalent metals, by the general formula, as we should now write it,



and that the group P_2O_7R'' was to be regarded as electro-negative to the group $P_2O_7Na_4$, so that the compound would be simply analogous to $ClNa$. If we write the double salt $P_2O_7R''Na_2$, we may regard the complex P_2O_7R'' as playing the part of a relatively electro-negative group, as in the case of double cyanides, so called. Whether this view is to be considered as identical with that of Persoz, is a question about which opinions may differ, and which is not important for my present purpose. Admitting that the groups P_2O_7R'' or P_2O_7R''' are transferable as such in their relatively simple alkaline salts, we may inquire whether they enter into the composition of complex acids, and if so, whether the compounds so formed differ from ordinary pyrophospho-tungstates and pyrophospho-molybdates. As the initial point in this investigation, I have selected mangano-disodic pyrophosphate, $P_2O_7Mn_2Na_2$.

Mangano-sodic Pyrophospho-Molybdate.

In another part of this memoir I have described several salts belonging to the group of pyrophospho-tungstates. As these were peculiar in their constitution, it became a matter of interest to determine whether the pyrophospho-molybdates had a similar constitution, or, in other words, whether they

contained the pyrophosphoric group $22\text{RO}_3 \cdot 9\text{P}_2\text{O}_7$, found in the salts of the tungstic series.

Molybdic tetroxide boiled with sodic pyrophosphate, care being taken to keep the oxide in excess, is dissolved with much facility, and in large quantity. The colorless solution may be evaporated to a syrup without yielding crystals on standing, and gives no precipitates with salts of potassium or ammonium. The solution, however, gives precipitates with salts of most of the heavier metals. Of these I selected the manganous compounds for special study, supposing that all the manganese would be present as base, and that a comparison could be made between salts of this type and those in which manganese exists in the pyrophosphoric molecule, and which I shall describe further on.

When a solution of manganous chloride is mixed with one of sodic pyrophospho-molybdate prepared as above, a dull buff-colored, apparently amorphous, precipitate is formed. On standing, with an excess of the sodium salt, this was gradually converted into a mass of beautiful bright yellow crystals. These were well washed with cold water, and then dissolved in boiling water. The filtered solution gave, on cooling, a mass of sulphur-yellow crystals, which were again dissolved and recrystallized. The salt was then dried on woolen paper. It was analyzed by Mr. G. W. Patterson.

{ 1.3289 grams gave 0.1065 gram P_2O_7 , $\text{Mg}_2 = 5.13$ per cent. P_2O_6 .

{ 1.3289 grams gave 0.2486 gram P_2O_7 , $\text{Mn}_2 = 9.36$ per cent. MnO .

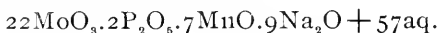
{ 0.9538 gram gave 0.1819 gram P_2O_7 , $\text{Mn}_2 = 9.53$ per cent. MnO .

{ 0.9538 gram gave 0.5934 gram $\text{P}_2\text{O}_6 + \text{MoO}_3 = 62.22$ per cent.

1.0960 grams lost with Wo_4Na_2 0.2037 gram = 18.56 per cent.

0.9445 gram lost with Wo_4Na_2 0.1743 gram = 18.45 per cent.

The analyses lead to the formula



which requires:

		Calculated.		Found.
22MoO ₃	3168	57.26	} 62.39	57.16
2P ₂ O ₅	284	5.13		5.13
7MnO	497	8.99	} 19.07	9.36
9Na ₂ O	558	10.08		9.84
57H ₂ O	1026	18.54		18.58
	<hr/>	<hr/>		
	5533	100.00		18.45

The salt is nearly insoluble in cold water. Boiling water dissolves it, but the salt is decomposed, giving a pale yellow flocky precipitate and a sherry-wine colored solution. On standing a short time, the solution, as it cools, becomes pale yellow, and finally almost colorless, while the precipitate gradually becomes brighter yellow and crystalline, and the original salt appears to be again formed by recombination. Both the precipitate formed in the decomposition by boiling water and the wine-yellow solution, give reactions with argentic nitrate which differ from one another, as well as from the yellow crystalline silver salt formed by digesting the pyrophospho-molybdate of manganese and sodium with argentic nitrate.

In the analysis, the solution of the salt was boiled with mercurous nitrate and mercuric oxide. The precipitate contained only molybdic and phosphoric oxides, and was free from manganese. There is, therefore, reason for assuming, as I have done, that all the manganese is basic, and that none is present in the form of the molecule P_2O_7Mn .

Mangano-ammonic Pyrophospho-Molybdates.

When manganous pyrophosphate is digested for some time with a strong solution of 14:6 acid ammonic molybdate, a buff-yellow, very slightly soluble, compound is formed. This is to be well washed, dried on woolen paper, and afterward *in pleno* over sulphuric acid. Of this salt, analyzed by Mr. G. W. Patterson,

0.7830 gram lost on ignition with WO_4Na_2 0.0778 gram NH_3
 $+ H_2O = 9.94$ per cent.

0.6554 gram lost on ignition with WO_4Na_2 0.0645 gram NH_3
 $+ H_2O = 9.84$ per cent.

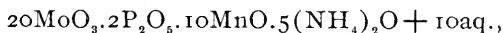
0.8590 gram gave 0.0338 gram $NH_3 = 3.92$ per cent.

0.7191 gram gave 0.0285 gram $NH_3 = 3.97$ per cent.

{ 0.8725 gram gave 0.0881 gram $P_2O_7Mg_2 = 6.46$ per cent. P_2O_5 .

{ 0.8725 gram gave 0.2841 gram $P_2O_7Mn_2 = 12.62$ per cent. MnO .

The analyses lead to the formula



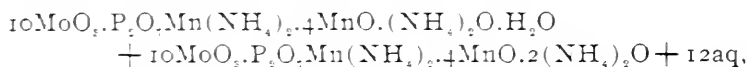
which requires:

		Calculated.		Found.
20MoO ₃	2880	66.76	} 73.34	67.27
2P ₂ O ₅	284	6.58		6.46
10MnO	710	16.46		16.30
10NH ₃	170	3.94	3.92	3.97
15H ₂ O	270	6.26		5.94
	<hr/>	<hr/>		
	4314	100.00		

In the analyses the salt was digested for some time at a boiling heat with mercurous nitrate and mercuric oxide. The mercurous salt formed contained manganous oxide. The precipitate was fused with a mixture of potassic and sodic carbonates to separate manganous oxide. The filtrate from this last gave the phosphoric pentoxide. Molybdic tetroxide was determined by difference. As the salt could not be recrystallized, the defects in the analysis are doubtless chiefly due to traces of impurity. The formula of the salt should be written, according to my view:



We may have here a double salt, as, for instance,



but of course other arrangements are possible.

The manganese in the molecule containing P₂O₅ may be called, for convenience, the internal or fixed manganese, to distinguish it from the external or basic manganese. To determine, if possible, the ratio between the external and internal manganese, I digested a weighed portion of the salt in the cold for twelve hours with mercurous nitrate, and then boiled, adding a little mercuric oxide in the usual manner. In the filtrate, after separating the mercury, the manganese was determined as P₂O₅·Mn₂. In this manner,

1.2306 grams gave 0.3520 gram P₂O₅·Mn = 11.08 per cent.

From this it appears that about $\frac{1}{10}$ of the manganese was precipitated by mercurous nitrate, in place of $\frac{8}{10}$. If, therefore, we consider $\frac{2}{10}$ of the manganese to be present in the salt as P₂O₅·Mn, we must suppose that this molecule is broken up, to a certain extent at least, by boiling with mercurous

nitrate, and it is very doubtful whether the manganous oxide exists in any other form than as a base. Certainly there is no sufficient evidence that it forms here an integrant molecule P_2O_7Mn , as in sodio-manganous pyrophosphate, $P_2O_7Mn.Na_2$. I regard the question, however, as still an open one, since the molecule P_2O_7Mn , assuming its existence, may be decomposed by mercurous nitrate and give a corresponding mercurous integrant molecule $P_2O_7Hg_2$, and since the salt is decomposed by water like the other salts of this series. It appears also from the above that the pyrophospho-molybdates do not correspond in composition to the pyrophospho-tungstates. At least I have not found in them the molybdenum molecule corresponding to the tungstic molecule, $22WO_3.9P_2O_7$. It must, however, be remarked that, as I shall show, the pyrophospho-tungstates which contain manganese do not contain this molecule.

Mangano-sodic Pyrophospho-Tungstates.

These salts are very easily formed by boiling manganous pyrophosphate with acid tungstates. Dark sherry-wine colored solutions are formed, which, in cooling, deposit crystals in abundance.

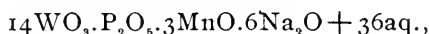
14:1:3:6 *Mangano-sodic Pyrophospho-Tungstate.* — This salt is formed more conveniently by mixing a solution of 12:5 sodic tungstate with manganous pyrophosphate and digesting for some hours in a closed bottle heated in a water-bath. The pyrophosphate must be in excess. It dissolves rather slowly to a fine deep orange-colored liquid, which after evaporation deposits beautiful crystals, which may be redissolved and recrystallized. In spite of the employment of an excess of manganous pyrophosphate, it is rather difficult to obtain a solution of the salt which is perfectly saturated with the manganous salt. The crystals have a brownish-orange color. They effloresce in dry air, though not rapidly, but *in pleno* over sulphuric acid they lose water in relatively large quantity. Of this salt, analyzed by Mr. G. W. Patterson,

1.4176 grams lost on ignition with WO_3Na_2 0.2032 gram = 14.34 per cent. water.

1.2375 grams gave 0.0611 gram $P_2O_7Mg_2$ = 3.16 per cent. P_2O_5 .

$\left\{ \begin{array}{l} 1.0476 \text{ grams gave } 0.1041 \text{ gram } P_2O_7Mn_2 = 4.97 \text{ per cent.} \\ \text{MnO.} \\ 1.0476 \text{ grams gave } 0.7650 \text{ gram } WO_3 + P_2O_5 = 73.05 \text{ per} \\ \text{cent.} \end{array} \right.$

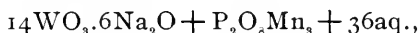
The analyses lead to the formula



which requires:

		Calculated.		Found.
14WO ₃	3248	70.25	} 73.32	69.89
P ₂ O ₅	142	3.07		3.16
3MnO	213	4.62	} 12.66	4.97
6Na ₂ O	372	8.04		7.68
36H ₂ O	648	14.02		14.34
	<hr/> 4623	<hr/> 100.00		

We may give this salt the formula

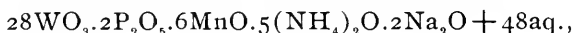


if we suppose that the pyrophosphate of manganese has become orthophosphate. Both constituents are then normal salts.

The ammonium salt was prepared by double decomposition between the sodium salt and ammonic chloride, and repeated crystallization. It presented orange-colored prismatic crystals, very soluble both in hot and cold water. Of this salt:

0.7846 gram gave 0.01715 gram NH₃ = 2.19 per cent.
 0.6556 gram gave 0.01394 gram NH₃ = 2.13 per cent.
 0.4886 gram gave 0.0594 gram NH₃ + H₂O = 12.16 per cent.
 1.0895 grams gave 0.1162 gram P₂O₅Mn₂ = 5.83 per cent. MnO.

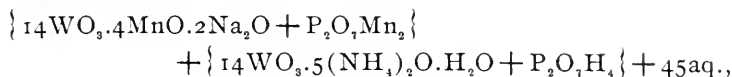
The analyses correspond well with the formula



which requires:

		Calculated.	Mean.		
28WO ₃	6496	77.67	77.76	77.84	77.69
2P ₂ O ₅	284	3.40	3.13	3.13	
6MnO	426	5.09	5.39	5.33	5.45
10NH ₃	170	2.03	2.16	2.13	2.19
2Na ₂ O	124	1.48	1.56	1.56	(diff.)
48H ₂ O	864	10.33	10.00	10.00	
	<hr/> 8364	<hr/> 100.00			

We may formulate this salt as



the type being $14\text{WO}_3.6.\text{RO} + \text{P}_2\text{O}_7\text{R}'_4$, so that so far as the empirical constitution is concerned the salt may be regarded as a double salt of two normal constituents. The analyses were made by Mr. G. W. Patterson.

[To be continued.]

DIAZOBENZENE ANILINE CHLORIDE.

BY J. H. KASTLE AND B. C. KEISER.

In the hope of obtaining diazobenzene chloride it occurred to one of us (Kastle), some years ago, to try the action of nitrosyl chloride upon aniline hydrochloride. Several experiments were made with these reagents, as a result of which a substance containing chlorine was obtained which, in many respects, resembled the other salts of diazobenzene. Notwithstanding the promise of these preliminary experiments, the investigation could not be carried out at that time and it was not until last summer that work along this line could be resumed. We have obtained as the result of our study of this reaction, not diazobenzene chloride, but a double salt of the same with aniline hydrochloride—that is, a compound whose composition and nature are probably to be represented by the formula $\text{C}_6\text{H}_5.\text{N}_2.\text{Cl} : \text{ClH}_3\text{N}.\text{C}_6\text{H}_5$.

Such a conclusion, we believe, to be warranted by the following observations :

Action of Nitrosyl Chloride on Aniline Chloride.

Nitrosyl chloride, prepared in the usual manner by treating nitrosyl sulphate with perfectly dry common salt, was passed into a thick paste of aniline hydrochloride and water. The vessel containing the mixture was surrounded by a freezing mixture of ice and salt. It was found that under these conditions action took place readily between the nitrosyl chloride and aniline hydrochloride, the latter going into solution in the

small quantity of water present, forming a dark, dirty-green or reddish-brown solution. The solution thus obtained was found to undergo decomposition very readily—so readily that in but few instances was it found expedient to pass in the quantity of gas required by the theory; and when this was done the yield was much smaller than from those batches which were exposed to smaller quantities of the gas. The best results were obtained with from one-half to two-thirds the theoretical quantity of nitrosyl chloride.

The solution obtained as above described was mixed with about an equal quantity of cold absolute alcohol and cold absolute ether added in small quantities at a time. After each addition of ether the vessel containing the substance was shaken while surrounded with cracked ice. After a time a white crystalline precipitate made its appearance which was found to increase in bulk up to a certain limit with each fresh portion of ether added. The precipitate was filtered off with the aid of a pump and washed with a small quantity of ether. The substance thus obtained certainly possesses the general characteristics of a diazo-compound. Frequently during the course of the investigation it was obtained in well-defined needle-shaped crystals, which became green, then pink, and, finally, brown in color on exposure to the air. It dissolves freely in water and in alcohol forming green solutions which rapidly change to red upon boiling or standing exposed to the air. The substance explodes when heated to 105° or over, giving off nitrogen and small quantities of hydrochloric acid.

A combustion-analysis of the compound was attempted; owing, however, to the explosions taking place in the tube no satisfactory results could be obtained.

On boiling the compound with water it was observed that only a portion of the nitrogen could be expelled; hence, in order to determine the percentage of this element in the compound, a small quantity of the substance was boiled with water in a small flask from which the air had been expelled by carbon dioxide. The nitrogen thus evolved was collected over caustic potash. The fixed nitrogen was determined as follows: A small portion of the substance was boiled with water in a Kjeldahl flask, the water expelled, and a Kjeldahl determination made of the residue.

The chlorine was determined by the usual gravimetric and volumetric methods. The following are the results for nitrogen and chlorine :

	I.	II.	III.	IV.	Calculated for $C_6H_5.N_2.Cl:$ $ClH_3N.C_6H_5.$
Diazo nitrogen ¹				11.01	10.27
Fixed nitrogen ²				4.96	5.18
Chlorine	24.85	25.38	25.44	24.91	26.29

The above figures for the nitrogen, together with the fact that two-thirds of the total quantity of this element present is driven off by simply boiling with water while the other one-third is retained, go to prove that the substance is not diazobenzene chloride.

These figures and facts, however, do prove conclusively that the compound contains a diazo residue and also a nitrogenous residue which is not of a diazo nature. The figures for the nitrogen agree fairly well for the double salt $C_6H_5.N_2.Cl = ClH_3N.C_6H_5.$ The numbers obtained for the chlorine agree better for diazobenzene chloride than they do for the double salt. The significance of these results will be discussed farther on.

Action of Water on the Compound.

About forty grams of the substance were dissolved in a liter of water and the solution heated to boiling. Decomposition took place very readily and large quantities of nitrogen were evolved. The solution was allowed to cool and was then filtered to remove a small quantity of resinous matter which had been formed during the decomposition. The filtered liquid was rendered decidedly alkaline with caustic soda and shaken up with ether; the ethereal layer was then separated from the alkaline liquid by means of a separating-funnel, and the ether allowed to evaporate spontaneously, whereby a reddish-brown oil having the odor of aniline was obtained. A small quantity of the oil, dissolved in concentrated sulphuric acid and treated with a small crystal of potassium bichromate, gave the magnificent blue color characteristic of aniline. The

¹ By "diazo nitrogen" is meant that portion expelled as free nitrogen on boiling the compound with water.

² By "fixed nitrogen" is meant that portion remaining in the compound after expulsion of the diazo nitrogen.

greater portion of the oil was treated with hydrochloric acid. The highly colored chloride thus obtained was purified with animal charcoal and recrystallized from water. It was finally obtained in colorless transparent crystals which gave the following numbers for chlorine on analysis:

	Found.	Calculated for $C_6H_5.NH_2.HCl$.
Cl	27.49 per cent.	27.41

The alkaline fluid left after separation of the ethereal layer containing the aniline, was then acidified with hydrochloric acid and again extracted with ether; the ether was separated as above and allowed to evaporate spontaneously. There was left behind an oily substance having the general characteristics of phenol. It responded to the usual tests for phenol with ferric chloride, etc., and on treatment with nitric acid it gave othonitrophenol which was identified by its color, odor, and melting-point.

By decomposition with water, therefore, the compound obtained by the action of nitrosyl chloride on aniline chloride yields phenol and aniline hydrochloride.

The Substance Yields Phenylhydrazine on Reduction.

In view of the fact that phenylhydrazine is very easily prepared by the reduction of a solution of diazobenzene chloride with stannous chloride, we were naturally led to try the action of stannous chloride upon a solution of the new compound. 5-10 grams of the substance were dissolved in a small quantity of water, and to this solution, kept cold by surrounding the flask containing it with cracked ice, was added the theoretical quantity of stannous chloride dissolved in concentrated hydrochloric acid. Immediately upon mixing these solutions the mass became solid. In order to remove the small quantity of liquid adhering to the crystals the mass above obtained was filtered. The residue was mixed with water, treated with an excess of caustic soda, and extracted with ether. The ether extract was allowed to evaporate spontaneously, whereby a reddish-brown oil was obtained which was then treated with an excess of concentrated hydrochloric acid. Two chlorides were thus obtained, one soluble, the other

insoluble, in an excess of the concentrated acid. The latter was purified by dissolving in a small quantity of water and reprecipitating with concentrated hydrochloric acid. The substance was thus obtained in the form of beautiful pearly white crystals identical in appearance, solubility in water and concentrated hydrochloric acid, and in chemical conduct with phenylhydrazine hydrochloride. Dilute aqueous solutions of it were found to reduce solutions of gold, platinum, silver, and mercury salts with remarkable ease.

The other chloride formed in this reduction, *viz.*, the one soluble in concentrated hydrochloric acid, was recovered and shown to be aniline hydrochloride. Hence, by reduction of the new compound, with stannous chloride, phenylhydrazine hydrochloride and aniline hydrochloride are obtained.

The Substance Forms a Double Salt with Platinum Chloride.

A concentrated aqueous solution of the new diazo derivative was treated with a strong solution of platinum chloride containing a small quantity of concentrated hydrochloric acid. A beautiful double salt was thus obtained in the form of golden-yellow crystals. In order to determine the platinum a weighed quantity of the substance was heated in a covered platinum crucible and the spongy platinum weighed. It gave the following result :

	Found.	Calculated for $C_8H_5.N_2.Cl:C_1H_3N.C_6H_5.PtCl_4.$
Pt	32.15	32.12

Synthesis of the Compound by Means of Diazobenzene Chloride and Aniline Hydrochloride.

In view of the fact that both the decomposition of the compound by water and its reduction by means of stannous chloride indicate that it contains a diazobenzene and an aniline residue it was thought that possibly the substance might be prepared synthetically by bringing together solutions of diazobenzene chloride and aniline hydrochloride, containing the required quantities of each of these substances. In order to test the correctness of this supposition the following experiment was tried: 9 grams of aniline hydrochloride were dis-

solved in the smallest possible amount of water and to this solution, well cooled by a freezing-mixture, there was added the theoretical quantity of a concentrated solution of potassium nitrite and also hydrochloric acid. About 20 cc. of absolute alcohol were then added together with about the same quantity of ether. The potassium chloride which was thus precipitated was removed by filtration, and to the filtrate containing the diazo-benzene chloride there were added 9 grams of aniline hydrochloride in solution in water and alcohol. Cold absolute ether was then added in small quantities at a time as long as any precipitate was produced.

There was obtained in this way quite a quantity of a substance identical in every respect with that obtained by the action of nitrosyl chloride on aniline hydrochloride. When first obtained, the substance is white, rapidly passing on drying through complimentary shades of green and pink. It dissolves freely in water giving a pale green solution which rapidly changes to red on boiling, with evolution of nitrogen when heated to 105° or over, the dry substance explodes with evolution of nitrogen and small quantities of hydrochloric acid gas. On analysis it gave the following numbers for nitrogen and chloride:

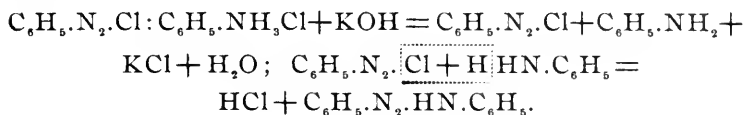
	Found.	Calculated for $C_6H_5 \cdot N_2 \cdot Cl : CH_3N \cdot C_6H_5$.
Diazo nitrogen	10.88	10.27
Fixed nitrogen	4.68	5.18
Chlorine	25.13	26.29

The above numbers for the nitrogen agree fairly well with those demanded by the theory. The want of exact agreement in the case of the chlorine is doubtless to be accounted for partly by the fact that, on standing, the compound undergoes a slight decomposition whereby a small quantity of hydrochloric acid escapes. This was proven by allowing a small quantity of the substance to remain for some time in moist air; the substance was found to deliquesce and silver nitrate gave a marked turbidity when shaken with the air in which the substance had been allowed to stand. Again, the formation of any benzene chloride—and it is more than probable that this substance would be formed by the spontaneous

decomposition of the compound—would cause a decrease in the quantity of chlorine obtained by the usual methods of simple precipitation with silver nitrate.

On Treatment with Caustic Potash the Substance Yields Diazoamidobenzene.

Another line of proof regarding the nature of the substance here at hand remained to be tested. It is well known that diazoamidobenzene is usually prepared by treating a salt of diazobenzene with aniline; hence if this compound contains both a diazobenzene and an aniline residue it ought to yield diazoamidobenzene when treated with one molecule of caustic potash, thus :



In order, therefore, to determine the possibility of such a reaction as this with the new compound several grams of the substance, prepared by the action of nitrosyl chloride upon aniline chloride, were dissolved in water and treated with the required quantity of caustic potash. Action took place at once, and a brownish-yellow precipitate was obtained which, on purification with animal charcoal and recrystallization from alcohol, was obtained in yellow crystals. It was found to be almost insoluble in water and readily soluble in hot alcohol from which it crystallized on cooling. It melted at 97° (uncorrected). So close is the agreement between the properties observed for this substance and those of diazoamidobenzene as usually prepared that there can be no doubt as to its identity with diazoamidobenzene.

Similar results were reached by treating the compound made from diazobenzene chloride and aniline hydrochloride with caustic potash.

Conclusion Regarding the Nature of the Substance.

As shown in the above the following points have been clearly established regarding the nature of the substance herein described :

1. It yields phenol and aniline chloride on decomposition with water.

2. It yields phenylhydrazine and aniline hydrochloride on reduction with stannous chloride.

3. It yields diazoamidobenzene on treatment with one molecule of caustic potash.

4. It has the general appearance and properties of a diazo compound. It changes color on drying and explodes when rapidly heated. It is not as explosive, however, as the salts of diazobenzene.

5. On boiling with water it gives off two-thirds, and only two-thirds, of its nitrogen.

6. It yields a crystalline platinum double salt with platinum chloride, containing 32.15 per cent. of platinum.

7. The substance itself can be prepared after the manner of double salts. (See p. 95.)

In the light of these facts we have been led to regard this compound as a double chloride of diazobenzene and aniline, and to call it diazobenzene-aniline chloride. It would certainly seem reasonable to suppose that a double salt of this nature, $C_6H_5.N_2.Cl:ClH_5N.H_5C_6$ could be prepared by the method described on p. 95; and that, in all probability, it would conduct itself towards water, reducing agents, and caustic potash as did the substance above described.

Some few attempts have been made to obtain analogous derivatives with the toluidines, without success. It is hoped, however, that by further study we may be able to obtain other double salts of this nature.

STATE COLLEGE OF KENTUCKY, LEXINGTON,
December, 1894.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

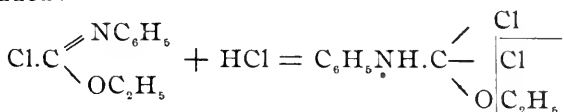
ON IMIDO-ETHERS OF CARBONIC ACID.

BY FELIX LENGFELD AND JULIUS STIEGLITZ.

In the course of an investigation on the action of phosphorus pentachloride on phenylurethane,¹ we found that ethylanilidochlorformate treated with dry hydrochloric acid gives ethyl chloride and chlorformanilide. Certain reac-

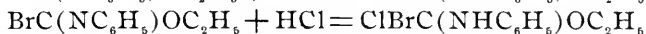
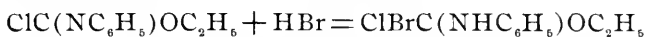
¹ This Journal, 16, 70.

tions¹ made us think that probably hydrochloric acid was first added :

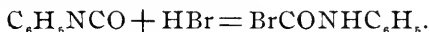


and that the addition-product decomposed as indicated. This is one of a number of reasons for suspecting that the chlorides of the imido-ethers, which suffer this same decomposition on heating, more or less, may not have the constitution RC(OR)(NRHCl) usually ascribed to them, but RCCl(NHR)(OR) .

We were unable to isolate the supposed intermediate chloride of ethylanilidochlorformate as it seemed to decompose even at -15° . To further test the above view we have tried the action of hydrobromic acid on ethylanilidochlorformate and of hydrochloric acid on ethylanilidobromformate. This allowed us to follow closely the course of the halogen atom originally in the ether and of that originally in the acid. In both reactions the intermediate products would be the same, if our views proved correct, and probably would show a behavior allowing this to be recognized.



Bromformanilide, $\text{BrCONHC}_6\text{H}_5$.—Qualitative tests showed that, when dry hydrobromic acid gas acts on ethylanilidochlorformate, both ethyl chloride and bromide are given off, leaving a mixture of chlorformanilide and bromformanilide. As the latter had never been obtained, we prepared some of the pure substance by passing dry hydrobromic acid over freshly distilled phenyl isocyanate :



The gas is rapidly absorbed, crystals being formed on the surface; to melt this crust and complete the reaction, the mixture is repeatedly warmed to 50° – 60° in the current of the gas. By powdering under dry petroleic ether, filtering, washing with petroleic ether, and bringing on a clay plate into a vacuum desiccator, white crystals of bromformanilide were

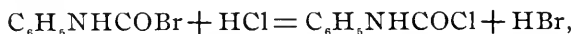
¹ *Ibid.*, 75, 76.

obtained. It has the same penetrating odor of phenyl isocyanate as chlorformanilide, melts at 67° (heated rapidly) and decomposes at 85° – 100° into hydrobromic acid and phenyl isocyanate.

Analysis.—0.2805 gram substance (heated with lime) required 14 cc. $\frac{N}{10}$ AgNO_3 solution (Volhard).

	Calculated for $\text{C}_7\text{H}_5\text{NOBr}$.	Found.
Br	40.00	39.93

As it was essential to know whether hydrochloric acid converts bromformanilide into chlorformanilide giving hydrobromic acid:



one gram of freshly prepared bromformanilide dissolved in 7.5 cc. cold absolute ether, was treated with 2.5 cc. ethereal hydrochloric acid (7.5 per cent. solution). After twenty minutes the ether was evaporated in a vacuum, the residue washed with a little ligroin and dried as usual. 0.241 gram substance heated with lime required 11.68 cc. $\frac{1}{10}$ N- silver nitrate.

Calculated for $\text{C}_7\text{H}_5\text{NOCl}$.	Calculated for $\text{C}_7\text{H}_5\text{NOBr}$.	Found.
15.5 cc.	12.05 cc.	11.68 cc.

Freshly prepared chlorformanilide treated in the same way with ethereal hydrobromic acid gave:

0.32715 gram silver halide obtained after combustion with lime, was reduced, giving 0.2444 gram silver.

	Calculated for AgCl .	Calculated for AgBr .	Found.
Ag	75.26	57.44	74.71

Both of these experiments show that there is practically no action under these conditions.

In order to obtain ethylanilidobromformate as required for this work, we first prepared:

Phenylimido-carbonyl Bromide, $\text{C}_6\text{H}_5\text{N}:\text{CBr}_2$.—Nef¹ found that phenyl isocyanide absorbs bromine, probably forming the compound, but did not examine the product any further. It can be obtained as follows: 10 grams (1 molecule) phenyl isocyanide, freshly distilled in a

¹ Ann. Chem. (Liebig), 270, 270.

vacuum, was dissolved in about 70 cc. of chloroform, from which every trace of water and alcohol had been carefully removed. The solution was cooled to -10° and 15.5 grams bromine (1 molecule), dissolved in 3 to 4 volumes of chloroform slowly added through a dropping funnel. A sudden change of color from blue to brownish-green took place when the calculated amount of bromine had been added and marked the end of the reaction. After twenty minutes, the chloroform was distilled off in a fractionating bulb under diminished pressure at 30° – 40° in a current of dry air. The oily residue distills without decomposition in a vacuum. The temperature rapidly rose to 123° and then very soon to 128° – 128.5° where it remained constant (at 20 mm.) during the greater part of the operation. An orange-colored oil distilled without any apparent decomposition, just as in distilling phenylimido carbonyl chloride, the cork was slightly attached, and probably caused the coloration. After refractionating, the portion boiling at 127° at 18 mm. was analyzed.¹

0.1910 gram gave 0.2577 gram silver bromide.

	Calculated for $C_7H_5NBr_2$.	Found.
Bromine	60.83	57.42

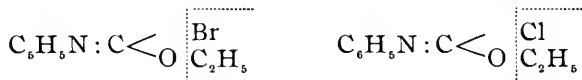
Phenylimidocarbonyl bromide has an odor similar to that of phenylimidocarbonyl chloride, but acquires easily a faint odor of phenyl isocyanide as well. It was converted by means of sodium ethylate into:

Ethylanilidobromformate, $C_6H_5N : CBr(OC_2H_5)$. — Phenylimidocarbonyl bromide (1 molecule) was treated with (1 molecule) sodium ethylate in absolute alcoholic solution just as described by us² for treating phenylimidocarbonyl chloride. An oil was finally obtained which was at first slightly reddish but soon became darker. It had an odor like ethylanilidochlorformate, but also a strong odor of phenyl isocyanide. By warming to 90° – 95° at 17 mm. most of the isocyanide was distilled off. On attempting to distill the oil remaining, it decomposed largely into ethyl bromide and phenyl isocyanate. As this prevented the purification of the ethylanilidobromformate for analysis, we determined the nature of the main part

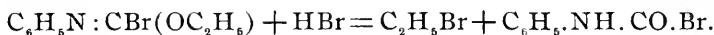
¹ NOTE.—Analysis made according to Carius by W. R. Smith.

² This Journal, 16, 73.

of the product as follows: Heat decomposes it into phenyl isocyanate and ethyl bromide, just as the corresponding chlorine compound gives phenyl isocyanate and ethyl chloride.¹



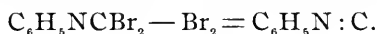
and hydrobromic acid gives ethyl bromide and bromformanilide:



As will be seen below, for our purposes there was no objection to the use of the crude product. Sodium alcoholate acts, as shown, partly according to the equation,



and partly removes bromine, regenerating phenyl isocyanide,



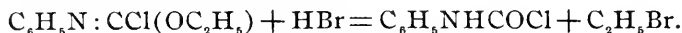
On treating phenylimidocarbonyl bromide with aqueous sodic hydrate, a strong odor of phenyl isocyanide is also evolved. The bromide appears to be less stable than the chloride.

Action of Hydrobromic Acid on Ethylanilidochlorformate.—To 1.5 gram (1 molecule) of ethylanilidochlorformate dissolved in absolute ether was added an equivalent quantity of ethereal hydrobromic acid (1 molecule) in a freezing-mixture. After thirty minutes the ether was removed by the vacuum pump at 0°, and the residue treated with dry petroleic ether, filtered, washed rapidly, and placed on a clay plate in a vacuum desiccator. An analysis of the haloformanilide, $\text{XCONHC}_6\text{H}_5$, showed that it was chlorformanilide.

Analysis.—Some of the substance was heated with lime, which was dissolved in nitric acid and treated with silver nitrate; a weighed quantity of the silver halide obtained, was reduced to silver. 0.2359 gram silver halide gave 0.1776 gram silver.

	Calculated for AgCl.	Found.
Ag	75.26	75.285

The reaction that took place is:



¹ This Journal, 16, 74.

Qualitative tests having shown that, in the action of gaseous hydrobromic acid on ethylanilidochlorformate ethyl chloride, ethyl bromide, chlor- and bromformanilide are formed, the quantitative course of the action was determined by estimating the proportion of ethyl chloride and bromide as follows: Freshly distilled ethylanilidochlorformate was used, prepared as described in our previous paper and having the boiling-point 103° – 104° at 17–18 mm.¹ The hydrobromic acid used was previously prepared from bromine, red phosphorus, water and potassium bromide and collected over mercury in bottles. For the determination it was, by means of mercury, made to pass in a slow current through a long calcium chloride tube and then into a small tube containing about one gram of the ethylanilidochlorformate, which was kept immersed in cold water. The gases then passed through a short tube containing calcium chloride and then through two sets of Geissler's bulbs containing a ten per cent. solution of sodic hydrate tinged with methylorange and into a narrow combustion tube, about twenty inches long, filled with calcium oxide and heated to redness. A moderate excess of hydrobromic acid was used and then dry air slowly passed through the system for an hour while the bulbs of the Geissler apparatus were heated in water-baths to about 90° . In this way all the alkyl halide formed, and no other halogen compound passed into the combustion tube. The lime was dissolved in nitric acid, the halogens precipitated as silver halide and a weighed quantity of this reduced to silver, and from this the proportion of ethyl chloride and ethyl bromide calculated. The results are those of two different determinations.

Analysis.—I. 0.4971 gram silver halide gave 0.3366 gram silver, corresponding to 57.62 per cent. AgCl and 42.38 per cent. AgBr, *i. e.*, 10 molecules of ethyl bromide to 18 molecules ethyl chloride.

II. 0.4486 gram silver halide gave 0.3112 gram silver, corresponding to 66.93 per cent. AgCl and 33.07 per cent. AgBr, *i. e.*, 10 molecules of ethyl bromide to 26 molecules of ethyl chloride.

¹ In our first paper, This Journal, 16, 74, the boiling-point was given by mistake as 115° – 120° at 20 mm.; it should have been 105° – 106° .

Action of Hydrochloric Acid on Ethylanilidobromformate.—

As the purpose of this investigation only required the quantitative determination of the proportion of ethyl chloride and ethyl bromide evolved in this action, and our system of apparatus only allowed the alkyl halides to pass into the lime tube, we could use the crude ethylanilidobromformate from which most of the phenyl isocyanide had been removed in a dry current of air at 100° at 20 mm., and which contained as impurities, only polymerized phenyl isocyanide and traces of the isocyanide itself. The experiment was conducted just as described in the analogous reaction.

Analysis.—I. 0.36625 gram silver halide gave 0.21175 gram silver, corresponding to 98 per cent. silver bromide and 2 per cent. silver chloride, or 1 molecule of ethyl chloride to 37 molecules ethyl bromide.

II. 0.155 gram silver halide gave 0.0893 gram silver, corresponding to 99.05 per cent. silver bromide and 0.95 per cent. silver chloride, or 1 molecule of ethyl chloride to 80 molecules of ethyl bromide. Therefore, what is given off is essentially ethyl bromide.

We see that the action of hydrobromic acid on ethylanilidochlorformate depends apparently on the conditions; in ethereal solution we have chiefly:

I. $C_6H_5N:CCl(OC_2H_5) + HBr = C_6H_5NHCOC l + C_2H_5Br$; and with gaseous hydrobromic acid, besides I, to a somewhat greater extent also:

II. $C_6H_5N:CCl(OC_2H_5) + HBr = C_6H_5NHCOBr + C_2H_5Cl$.

Hydrochloric acid gas acts on ethylanilidobromformate almost entirely according to:

III. $C_6H_5N:CBr(OC_2H_5) + HCl = C_6H_5NHCOC l + C_2H_5Br$; and to a slight extent according to:

IV. $C_6H_5N:CBr(OC_2H_5) + HCl = C_6H_5NHCOBr + C_2H_5Cl$.

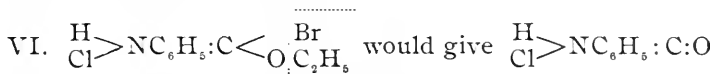
From these reactions the following conclusions may be drawn:

1°. From II and III giving the main actions we see there is not a simple removal of the alkyl by the acid according to:

V. $(C_6H_5N)XC.OC_2H_5 + YH = C_6H_5NHC OX + C_2H_5Y$.

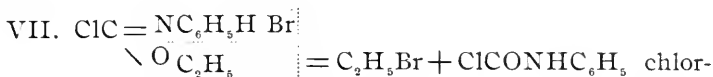
2°. The intermediate product, probably formed, can not

have the constitution $\begin{array}{c} \text{H} \\ \diagup \\ \text{Y} \end{array} > \text{NC}_6\text{H}_5 : \text{C} < \begin{array}{c} \text{X} \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array}$ usually ascribed to the halides of imido-ethers since, in the first place, according to reaction III:

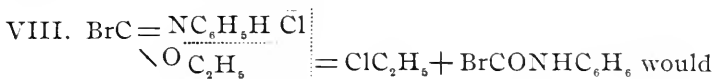


as the constitution of chlorformanilide (a so-called "urea-chloride"), whereas it is better expressed¹ by $\text{C}_6\text{H}_5\text{NHCOCl}$; —and since, in the second place, the loss of alkyl halide, taking place in the same way as the loss of alkyl chloride from the salts of the imido-ethers $\text{RC} \equiv \text{NRH} \begin{array}{c} \text{X} \\ \diagdown \\ \text{O} \cdot \text{C}_2\text{H}_5 \end{array}$ would give us

for II:

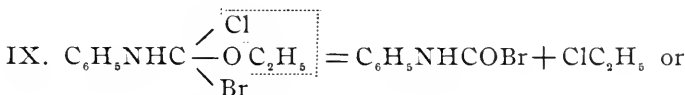


formanilide and ethyl bromide, while in fact the products with gaseous hydrobromic acid (equation II) are chiefly bromformanilide and ethyl chloride. Just so in III:

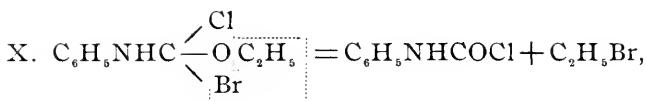


give us bromformanilide and ethyl chloride, while the actual products are nearly entirely ethyl bromide and chlorformanilide.

3°. The formation of the intermediate addition-product, $\text{C}_6\text{H}_5\text{NH} \cdot \text{C}(\text{OC}_2\text{H}_5)\text{ClBr}$, explains perfectly both the formation of haloformanilide of the constitution $\text{C}_6\text{H}_5\text{NHCOX}$, and the formation of the alkyl halides as actually found. We obtain then by the action of hydrobromic acid on ethylanilidochlorformate, and of hydrochloric acid on ethylanilidobromformate, the same addition-product which can decompose according to:



¹ Leuckart, Ber. d. chem. Ges., 18, 873; Gattermann, *Ibid*, 20, 118; and Ann. Chem. (Liebig), 244, 30.



according to the conditions obtaining in the experiment. With dry hydrobromic acid both IX and X occur. *With dry hydrochloric acid and ethereal hydrobromic acid, practically only reaction X takes place.* The given constitution of the intermediate product agrees best, therefore, with the actual behavior of the compounds, briefly:

1. The formation of the haloformanilides of the constitution $\text{C}_6\text{H}_5\text{NHCOX}$.

2. The formation in one reaction of both ethyl chloride and bromide, and the two acid anilides, chlor- and bromformanilide.

3. The formation of ethyl bromide only, when only one alkyl halide is given off, whether hydrobromic or hydrochloric acid is used. The question naturally arises why the addition-product, under apparently the same conditions when formed by the action of the dry gases, does not give absolutely identical decomposition-products. The conditions are, however, only apparently the same, and only as to external temperature, etc. The fact that with gaseous acids the halogen of the original ether is given off to a greater extent than the new halogen entering indicates forces at work in the molecule which we cannot subject to exact identity of condition. The conclusions drawn above are based on facts which exist independently of any such requirement.

As we could not isolate the addition-product, which forms so important a link in these reactions, we treated the corresponding phenylanilidochlorformate, $\text{C}_6\text{H}_5\text{N} : \text{CCl}(\text{OC}_6\text{H}_5)$, with gaseous hydrochloric acid in the expectation that the addition-product would not lose phenyl chloride and so would prove more stable. This was found to be so. A product, $\text{C}_6\text{H}_5\text{NH} \cdot \text{CCl}_2(\text{C}_6\text{H}_5)$, was obtained, in perfect agreement with the views expressed above.

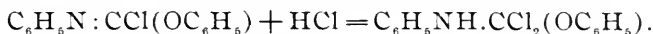
Phenoxyformphenylamidodichloride ($\text{C}_6\text{H}_5\text{O})\text{CCl}_2(\text{NHC}_6\text{H}_5)$.—Phenylanilidochlorformate was prepared from phenylimido-carbonylchloride and sodium phenolate, according to our

method for preparing the ethylate.¹ 1.5 grams phenyl-anilidochlorformate (M. p. 41°) was dissolved in 30 cc. petrolic ether (B. p. 30°–40°) and filtered from a slight residue of phenyl carbanilate. The filtrate was placed in a freezing-mixture and dry hydrochloric acid passed in. A white precipitate which formed was rapidly filtered, washed with petrolic ether, and brought on a clay plate in a vacuum desiccator.

Analysis.—0.1667 gram substance heated with lime required 12 cc. $\frac{N}{10}$ AgNO₃ solution (Volhard).

	Calculated for C ₁₃ H ₁₁ NOCl ₂ .	Found.
Cl	26.49	25.58

Phenoxyformphenylamidodichloride (a derivative of ortho-carbonic acid), softens at 60° and melts at 65° with decomposition. In the presence of moisture it yields phenyl carbanilate (M. p. 125°). It is formed according to the equation:



ADDITION OF HYDROCHLORIC ACID TO
CARBODIPHENYLIMIDE.

As we found² that carbodiphenylimide unites with ethyl alcohol to form ethylisodiphenylurea,



we thought we could, by means of this compound, decide whether the addition-product of hydrochloric acid to carbodiphenylimide is a salt, $C_6H_5N:C:NC_6H_5.HCl$, or, as seems probable, an imidechloride $C_6H_5N:C \begin{smallmatrix} Cl \\ \nearrow \\ NHC_6H_5 \end{smallmatrix}$.

Weith first found³ that carbodiphenylimide, when treated in benzene solution with hydrochloric acid, adds one molecule of the acid. He obtained a crystalline precipitate which a chlorine determination showed to be $(C_6H_5N)_2C.HCl$. Later he states⁴ that, on continuing the current of hydrochloric acid, the precipitate redissolved, and the solution, on standing, deposited distinct crystals, which he did not analyze, but took to be larger crystals of the same chloride, and this has passed into

¹ This Journal, 16, 73; and W. R. Smith, This Journal, 16, 392.

² Ber. d. chem. Ges., 27, 926.

³ *Ibid*, 7, 11.

⁴ *Ibid*, 9, 816.

the literature of the subject. On preparing the chloride for the above purpose, we analyzed the larger crystals and found that we had not a monochloride, but a dichloride.

Carbodiphenylimidedichloride, $C(NC_6H_5)_2 \cdot 2HCl$.—6 grams freshly prepared carbodiphenylimide (B. p. $187^\circ-8^\circ$ at 20–22 mm., after two fractionations) was dissolved in 120 grams pure dry benzene. When pure, both the oil and its solution are entirely colorless. On passing dry hydrochloric acid into the solution (not cooling) it remains clear for the first few minutes. Then a voluminous precipitate suddenly appears, apparently almost entirely taking the place of the liquid. On continuing the current, and rotating the flask to aid in the solution of hydrochloric acid, the mixture gradually clears up, and finally, almost everything goes into solution. Sometimes a few distinct transparent crystals remain undissolved.

The whole is allowed to stand over night, care being taken to exclude moisture. In the morning a large quantity of the transparent crystals is found deposited. The liquid is poured off, the crystals brought rapidly on a Hirsch funnel, washed with benzene, and brought on a clay plate into a vacuum desiccator over sulphuric acid, potassium hydrate, and vaseline. After twenty-four hours, the crystals for analysis were finely powdered and again placed in the vacuum desiccator for a day.

Analysis.—

1. 0.2163 gram substance, heated with lime, required 16.0 cc. $\frac{N}{10}AgNO_3$ solution (Volhard).
2. 0.2223 gram substance, heated with lime, required 16.33 cc. $\frac{N}{10}AgNO_3$ solution (Volhard)

	Calculated for $(C_6H_5N)_2C \cdot 2HCl$.	Found.	
		1.	2.
Cl	26.59 per cent.	26.26	26.08

The compound is, therefore, carbodiphenylimidedichloride. The crystals are thick, short prisms with pyramidal terminations, apparently tetragonal or orthorhombic. The substance begins to decompose and melt at 130° , the action becoming violent at 145° . It is, therefore, impossible to speak of a constant melting-point. When heated, a yellow substance, probably one of the carbodiphenylimides, remains, and a gas,

found to be hydrochloric acid, is given off. The dichloride is quite soluble in hot chloroform and is reprecipitated unchanged by ligroin. It is quite stable when kept from moisture or organic matter. In contact with these it loses hydrochloric acid. A specimen, kept ten days in a corked tube, attacked the cork somewhat and, on analysis, gave:

1. 0.2172 gram substance, heated with lime, required 15 cc. $\frac{N}{10}$ AgNO₃ solution (Volhard).

2. 0.3415 gram substance gave 0.3403 gram AgCl (Carius).

	Calculated for (C ₆ H ₅ N) ₂ C ₂ HCl.	Found.	
		1.	2.
Cl	26.59 per cent.	24.51	24.65

Boiled with water, or better, with aqueous alcohol, the dichloride gives carbanilide (M. p. 235°). In preparing the dichloride it is necessary to use, pure, freshly prepared liquid carbodiphenylimide. If solid carbodiphenylimide is present, hydrochloric acid colors the benzene solution yellow, and the crystals formed are more or less coated with a yellow sticky mass. The constitution of the dichloride has not been determined. It may be (C₆H₅NH)₂CCl₂ if the second molecule of hydrochloric acid adds in the same way as the first (see below), and it may be ClC(NC₆H₅)(NHC₆H₅)HCl, the chloride of chlorformdiphenylamidine. An attempt will be made to decide the question experimentally.

Carbodiphenylimidesesquichloride (?), [(C₆H₅N)₂C]₃HCl or (C₆H₅NH)₂CCl₂ + C₆H₅NHC(NC₆H₅)Cl. — The voluminous precipitate first formed, (see page 108), on passing hydrochloric acid into carbodiphenylimide in benzene solution likewise contains more chlorine than the monochloride. As soon as the voluminous precipitate is formed, the current is stopped and the precipitate treated as above. The result is the same, whether the mixture is cooled or not. A white mass, of pearly luster, remains on the clay plates. For analysis, this was powdered, and again put in the vacuum-desiccator for twenty-four hours. Analyses of five different preparations were made:

1. 0.2283 gram substance, heated with lime, required 14.4 cc. $\frac{N}{10}$ AgNO₃ solution (Volhard).

2. 0.2293 gram substance, heated with lime, required 14 cc. $\frac{N}{10}$ AgNO₃ solution.

3. 0.3051 gram substance, heated with lime, required 17.9 cc. $\frac{N}{10}$ AgNO₃ solution.

4. 0.1805 gram substance, heated with lime, required 10.08 cc. $\frac{N}{10}$ AgNO₃ solution.

5. 0.2047 gram substance, heated with lime, required 13.08 cc. $\frac{N}{10}$ AgNO₃ solution.

Calculated for (C₆H₅N)₂C.ClH = 15.4 per cent. Cl.

“ “ [(C₆H₅N)₂C]₂3HCl = 21.4 per cent. Cl.

“ “ (C₆H₅N)₂C.2HCl = 26.59 per cent. Cl.

	1.	2.	3.	4.	5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Found,	22.39	21.67	20.83	19.82	22.68

The substance may be a mixture of monochloride and dichloride in nearly molecular quantities. It was very frequently obtained and seems to have more or less characteristic properties by which it can be identified. It melts with decomposition at 115°–125°, the evolution of hydrochloric acid being strongest and completed at 150°. It is extremely soluble in cold chloroform and not insoluble in benzene.

*Carbodiphenylimidemonochloride or Chlorformdiphenylamidine.*¹

CIC (NHC₆H₅) (NC₆H₅).—Special precautions must be observed if only one molecule of hydrochloric acid is to be added to one molecule of di-imide. Weith says nothing regarding the details in the preparation of the monochloride which he analyzed² nor does he give any properties or physical constants by which it may be identified.

Only once in working as he did with a cold, concentrated benzene solution of the di-imide (5 grams in 3 or 4 volumes of benzene) did we obtain a compound whose analysis and behavior showed it to be, approximately, pure monochloride. As soon as a small quantity of precipitate was formed, the current of hydrochloric acid was stopped, the flask which had been kept in ice-water allowed to assume the temperature of the room, the precipitate washed with ligroin (B. p. 70°–80°), and

¹ The compound may be called carbanilide imidechloride, using Wallach's nomenclature (Ann. Chem. (Liebig), 184, 4). It is a representative of the true ureachlorides (carbamidechlorides) NH₂C(NH)Cl as distinguished from the chlorformamides which are sometimes incorrectly so called.

² Ber. d. chem. Ges., 7, 11.

treated as usual. The compound began to soften at 70° and had melted entirely at 110° . Analysis :

0.2644 gram substance required, when burned with lime,

11.83 cc. $\frac{N}{10}$ AgNO₃ solution (Volhard).

Calculated for (C₆H₅N)₂CHCl. Found.

Cl	15.40	15.88
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In a very large number of experiments, however, the precipitate formed by this method contained much more dichloride, and showed the properties of the mixture or sesquichloride described above. The pure monochloride was finally obtained as follows : 5 grams freshly-prepared di-imide was dissolved in 40-50 cc. ligroin (B. p. 40° - 60°), cooled in ice-water and hydrochloric acid led into the solution. A precipitate was at once formed, and, after a few moments, and before the precipitation was complete, the deposit was rapidly brought on a filter, washed with ligroin, and dried as usual. Analysis :

0.366 gram substance heated with lime, required

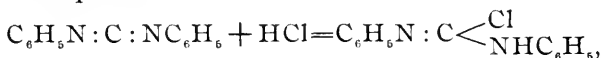
15.65 cc. $\frac{N}{10}$ AgNO₃ solution (Volhard.)

Calculated for (C₆H₅N)₂CHCl. Found.

Cl	15.40	15.18
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Chlorformdiphenylamidine (carbodiphenylimidechloride) melts completely at 92° - 95° with slight evolution of gas, this increasing on raising the temperature. It is readily soluble in chloroform and benzene, and reprecipitated by ligroin. The presence of dichloride raises its melting-point. On treating the filtrate from the chlorformdiphenylamidine with more hydrochloric acid a heavy precipitate was formed. Analysis showed this to be a mixture of di- and monochloride. Even when only the calculated quantity (1 molecule) of hydrochloric acid (a measured volume of the gas or its ethereal solution) was added to a ligroin solution of the di-imide (1 molecule), the precipitate was a mixture of the two chlorides (containing 16.6 per cent. Cl instead of 15.4 per cent. as in monochloride), while the filtrate contained unchanged di-imide. In preparing pure chlorformdiphenylamidine the yield is small, as much less than the calculated amount of hydrochloric acid must be used. Carbodiphenylimidechloride gives, with sodium ethylate in the cold, ethyl-

isodiphenylurea, which makes it very probable that addition of hydrochloric acid to carbodiphenylimide takes place according to the equation



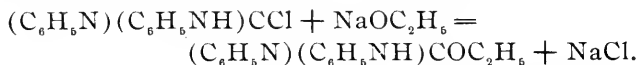
forming chlorformdiphenylamidine and not a simple salt of carbodiphenylimide, $\text{C}(\text{NC}_6\text{H}_5)(\text{NC}_6\text{H}_5\text{HCl})$.

Action of Sodium Ethylate on Chlorformdiphenylamidine.

Ethoxyformdiphenylamidine or Ethylisocarbanilide,



Six grams (1 molecule) chlorformdiphenylamidine was added in portions to a cold solution of sodium ethylate (0.6 gram sodium, 1 atom) in 15 grams absolute alcohol. After ten minutes it was poured into about a liter of cold water, extracted with ether, the ethereal solution washed 5 or 6 times with a little water, filtered, and dried for eighteen hours over anhydrous sodium sulphate. On distilling off the ether, an oil and a few crystals, identified as carbanilide, remained. The oil could be separated from the carbanilide by dissolving in ligroin. After removing the ligroin, the oil was distilled in a vacuum. The main fraction came over at 205° – 206° at 25 mm., and showed all the other properties of ethoxyformdiphenylamidine. It remains a mobile oil even after standing for some time, while carbodiphenylimide becomes thick and then solid. With dry hydrochloric acid, at 100° , it gave¹ ethyl chloride, burning with green-tinged flame, and carb-anilide, melting at 235° , $(\text{C}_6\text{H}_5\text{N})(\text{C}_6\text{H}_5\text{NH})\text{COC}_2\text{H}_5 + \text{HCl} = (\text{C}_6\text{H}_5\text{NH})_2\text{CO} + \text{C}_2\text{H}_5\text{Cl}$. The formation of the compound takes place according to the equation:



This reaction may be used to prepare the isoureaethers, the use of sealed tubes being thus avoided.

It is not necessary to isolate the chlorformdiphenylamidine, the best yield being obtained as follows:

Ten grams freshly prepared carbodiphenylimide is dissolved in 30 to 40 cc. absolute alcohol, the solution cooled in ice-

¹ Ber. d. chem. Ges., **27**, 927.

water, the calculated amount of ethereal hydrochloric acid (we used 9.5 cc. of a 20-per cent. solution) added, and the mixture poured into a cooled solution of sodium ethylate (1.2 grams sodium). After a few minutes the mixture is poured into cold water and treated as above. A good yield (7.5 grams) of ethylisocarbanilide was obtained as a colorless, mobile oil, which boiled at 205° – 207° at 25 to 26 mm.

This work shows that when hydrochloric acid is taken up by acid derivatives, $\text{XC} \begin{smallmatrix} \text{NC}_6\text{H}_5 \\ \text{OR} \end{smallmatrix}$ or $\text{Y}'' = \text{C} = \text{NC}_6\text{H}_5$ containing the phenylimide group, a double bond is opened and the group $\text{C} \begin{smallmatrix} \text{NHC}_6\text{H}_5 \\ \text{Cl} \end{smallmatrix}$ formed. Further work in this direction is being done.

ON SOME BROMINE DERIVATIVES OF PARAI-SO-BUTYL PHENOL.

BY F. B. DAINS AND I. R. ROTHROCK.

Monobromparaisobutyl Phenol.—When the dry sodium salt of *p*-isobutyl phenol is suspended in dry carbon bisulphide and bromine (1 molecule) added, the solution is soon decolorized with the separation of sodium bromide. After filtering and distilling off the carbon bisulphide a dark-colored oil is left. This is best purified by distilling with steam, which carries over a colorless aromatic oil, which, in turn, soon solidifies. The solid product may be dried on a clay plate and crystallized from low-boiling petroleum. From this solvent monobrom *p*-isobutyl phenol separates out in fan-like clusters of blunt needles, which melt at 50° . It is very easily soluble in ordinary organic solvents. Analysis:

0.2634 gram substance gave 0.2150 gram AgBr.

Found.	Calculated for $\text{C}_{10}\text{H}_{13}\text{OBr}$.
Br 34.73	34.93 per cent.

The same product can be obtained by treating the free *p*-isobutyl phenol dissolved in water or carbon bisulphide with the calculated amount of bromine.

The benzoyl ether of monobromparaisobutyl phenol was obtained by dissolving the phenol in caustic soda and adding the proper amount of benzoyl chloride. The solid formed was purified by crystallization from methyl alcohol and low-

boiling petroleum. The fine needle-like crystals melt at 78.5° .
Analysis :

0.2430 gram substance gave 0.1373 gram AgBr.

Found.	Calculated for $C_6H_3.Br.C_4H_9.OCO C_6H_5.$
Br 24.04	24.02 per cent.

Dibromparaisobutyl Phenol.—When *p*-isobutyl phenol (1 molecule) is treated with bromine (2 molecules) in water, carbon bisulphide, or acetic acid solution, there is formed the dibrom substitution-product. It is best purified by crystallization from ligroin, from which it separates out in large yellowish plates melting at 78° . These crystals are often very large. One of them was 30 mm. long, 22 mm. wide, and 6 mm. thick. The substance dissolves easily in organic solvents.
Analysis :

0.1590 gram substance gave 0.1946 AgBr.

Found.	Calculated for $C_6H_2.Br_2.OH.C_4H_9.$
Br 52.08	51.94 per cent.

When the phenol is treated in solution with an excess of bromine (3 or 4 molecules) the only definite product formed seems to be the dibromparaisobutyl phenol. Efforts were made to determine the position of the bromine atoms by oxidizing the isobutyl group to carboxyl, thus forming a derivative of *p*-hydroxybenzoic acid. Potassium bichromate and sulphuric acid, potassium permanganate in alkaline solution, and chromic acid in acetic acid solution, were found to break up the molecule completely, giving no benzoic acid.

It is exceedingly probable, however, from analogous reactions, that the bromine atoms are both ortho to the hydroxyl—thus giving an orthobromparaisobutyl phenol and a diorthobromparaisobutyl phenol.

ON THE ACTION OF ACID CHLORIDES ON THE METHYL ETHER OF PARISOBTUTYL PHENOL.

BY F. B. DAINS.

It has been shown by Gattermann¹ and others that phenol ethers react with acid chlorides in the presence of aluminum chloride, forming substituted ketones.

¹ Ber. d. Chem. Ges., **22**, 1129; **23**, 1199.

With a simple phenol ether, or with an ortho¹ or meta² substituted phenol ether, the entering radicle goes in the para position. It was thought to be of interest to investigate the action of acid chlorides upon para-substituted-phenol ethers.

This preliminary report is now published, since further work along this line must be deferred for a short time.

Ortho-methoxymetaisobutyl Acetophenone.

One part of the methyl ether of *p*-isobutyl phenol and one part acetyl chloride are dissolved in carbon bisulphide or, better, ligroin [B. p. 70°–80°] in a flask fitted with a reflux condenser, and two parts aluminum chloride slowly added. The reaction begins at once with evolution of hydrochloric acid. To complete the reaction the flask is heated on the water-bath. After cooling, the excess of solvent is poured off, and the black residue in the bottom of the flask is decomposed with water. The oil that separates out is taken up with ether, dried, and distilled. The bulk of the oil passes over between 262° and 265°, at 749 mm. When freshly distilled it is of a light yellow color, but soon assumes a greenish tinge. Analysis:

I. 0.2757 gram substance gave 0.7644 gram CO₂ and 0.2096 gram H₂O.

II. 0.2304 gram substance gave 0.6395 gram CO₂ and 0.1805 gram H₂O.

	Found.		Calculated for C ₆ H ₃ { OCH ₃ C ₄ H ₉ COCH ₃
	I.	II.	
C	75.62	75.69	75.73
H	8.44	8.71	8.74

Orthomethoxymetaisobutyl acetophenone does not solidify at –18°.

When this ketone is dissolved in alcohol, the proper amount of hydroxylamine hydrochloride and sodium carbonate added and the mixture allowed to stand, the corresponding ketoxime is formed. This was purified by dissolving in caustic soda. From the oil obtained, crystals separate out on standing in a desiccator. These dried on a clay plate and crystallized from ligroin form needles melting at 113°–114°. Analysis:

¹ Ann. Chem. (Liebig), **244**, 64. ² Ber. d. chem. Ges., **21**, 2270.

0.2208 gram substance gave 13.7 cc. N at 27° and 747 mm.

Found.	Calculated for $C_{13}H_{19}NO_2$.
N 6.78	6.34 per cent.

The Action of Benzoyl Chloride.

Orthomethoxyparaisobutyl Benzophenone.

8 grams of methyl ether and 7 grams of benzoyl chloride were dissolved in carbon bisulphide and 12 grams aluminum chloride added slowly. The dark-colored product of the reaction was decomposed with water, the oil taken up with ether, dried, and distilled. Above 315° there came over a light-colored oil which changed to a greenish color on standing. Analysis :

0.2768 gram oil gave 0.1863 gram H_2O and 0.8141 gram CO_2 .

	Found.	Calculated for $C_{18}H_{26}O_2$.
C	80.28	80.60
H	7.48	7.46

There is not much doubt that the entering acyl group is in the ortho position to the methoxy group. Gattermann has found, for instance, that *p*-cresolmethyl ether and urea hydrochloride under like conditions form orthomethoxymetatoluic acid amide.¹ This point will be proved experimentally later, and the action of acid chlorides on other para-substituted-phenol ethers and on mesitylol investigated.

THE EFFECT OF HYDROLYSIS UPON REACTION-VELOCITIES.²

BY F. L. KORTRIGHT.

In almost all of the cases where reaction-velocities in aqueous solution have been studied according to the "Mass Law" of Guldberg and Waage, the reactions have been between substances which are practically non-hydrolyzed and in these cases the amount of each substance actually taken for the experiment can be considered the *active mass*. When, how-

¹ Ann. Chem. (Liebig), 244, 66.

² In this article the term "hydrolysis" is employed instead of the more cumbersome term "hydrolytic dissociation," to indicate the decomposition of a salt in aqueous solution, into a base and an acid by the action of the water. The salt so decomposed is "hydrolyzed."

ever, one or more of the substances taking part in the reaction is hydrolyzed, the total amount of the substance used can not be taken as its *active mass*; only the non-hydrolyzed portion can be so considered. A case of this kind has recently been given by Kahlenberg¹ in an excellent experimental paper on the velocity of the reaction between ferric chloride and stannous chloride. Unfortunately, he has, however, calculated his results on the assumption that the *active mass* of the reacting substances is the total amount taken, while in reality, since ferric chloride and stannous chloride are strongly hydrolyzed, the *active mass* is much less. That this is true may be seen from the following considerations:

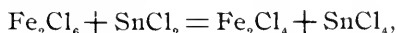
The generally accepted expression for the reaction-velocity in a bimolecular reaction, where the two substances are taken in equimolecular amounts, and the reaction goes as good as completely in one direction, is

$$dx/dt = c(a-x)^2 \quad (1)$$

where a represents the amount of substance present at the beginning, x the amount of substance which has been transformed during the time t , and c is the proportionality-factor. Integrating from 0 to t and noting that for $t=0$, $x=0$, there results

$$x/t(a-x) = ac = \text{const.} \quad (2)$$

If the reaction takes place according to the equation

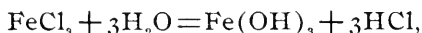


that is if the reaction takes place between the total amount of ferric chloride and stannous chloride present, then equation (2) should hold good and its left member should, at constant temperature, maintain a constant value. When the experimental data are substituted in equation (2) it gives, in the experiment where the conditions for hydrolysis are best, a value for $x/t(a-x)$ varying from 0.00921 to 0.00536 in 140 minutes and falling to 0.00421 at the end of 320 minutes, with a constant decrease from the upper to the lower value and, where the conditions for hydrolysis are poorest, a value varying from 0.0721 to 0.0468 in 130 minutes. In some experiments two or three consecutive values of the constant lie

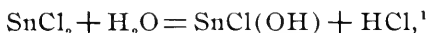
¹ J. Am. Chem. Soc., 16, 314.

closely together, but in these cases a plot of the curve expressing $x = \varphi(t)$ shows that these values fall off from the curve and are due to experimental error. This result must lead to the conclusion that either something is wrong with the experimental work or with the formula. The experimental values of $x = \varphi(t)$ form as smooth a curve as might be expected and, therefore, the trouble must be in the formula.

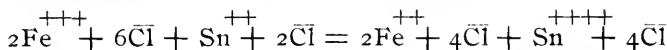
When ferric chloride is dissolved in water a reaction takes place between the water and the salt, in which the chlorine of a portion of the ferric chloride is replaced by the hydroxyl of the water, and hydrochloric acid is set free according to the equation



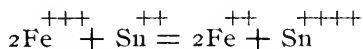
in which the ferric hydroxide is a soluble colloidal form which may be considered electrolytically undissociated. The remainder of the ferric chloride is almost entirely dissociated electrolytically into ferric and chlorine ions. In the same way there is a reaction between the water and the stannous chloride with the formation of basic tin chloride according to the equation



and the remainder is electrolytically dissociated into stannous and chlorine ions. Therefore in the solution at the beginning there are undissociated colloidal ferric hydroxide, basic tin chloride, a *small* amount of the undissociated salts, and ferric, stannous, chlorine, and hydrogen ions. Since, as is well known, all inorganic chemical reactions in aqueous solution seem to take place between the ions of the reacting substances, it is safe to conclude that here the reaction is not between the total amount of salts in solution, but merely between that amount of each which is present as ions. Upon this assumption the reaction may be written



or, since the $\bar{\text{Cl}}$ is the same on each side, we may write



¹ Kahlenberg found this hydrolysis to take place to such an extent that he was obliged to partially repress it by the addition of hydrochloric acid in order to keep his solution clear.

where the + and — marks have the significance usually assigned to them in reactions of this kind.

If the assumption that the reaction consists of a transfer of electrical charges from the ferric to the stannous ions, be correct, it is necessary to determine the concentration of these ions at the time t , in order to apply the "Mass Law" to a study of the velocity of the change.

The amount of undissociated salt is so small that it is possible to consider all except the hydrolyzed portion in the form of ions, and the problem resolves itself into finding an expression which will give a as a function of the hydrolysis at the time t .

Since tin and iron are nearly equally strong bases we may assume that they are equally effected by the water and since the experiments were carried out using equimolecular amounts of each salt, we may assume that the relation continues equimolecular, and by plating $x=\varphi(t)$ we can select a point where the curve becomes nearly parallel to the t axis and $(a-x)=h$ is approximately the amount of hydrolyzed substance at that time. Assuming that the hydrolysis is constant throughout the time of the experiment, (which is sufficiently correct for our purpose) the active mass at the beginning of the experiment becomes $(a-h)=a'$. By substituting this value for the initial *active mass* in equation (2), it gives

$$x/t(a'-x)=a'c=\text{const.} \quad (3)$$

In the following tables t is the time in minutes, x the amount of substance which has been transformed during the time t , ac is the value of $x/t(a-x)$ obtained from equation (2) and $a'c$ is the value of $x/t(a'-x)$ obtained from equation (3). Varying amounts of hydrochloric acid were added to the solutions in the experiments and this is indicated at the head of each table.

A description of the experimental method used in obtaining these results may be found in the article by Kahlenberg.¹

¹ Loc. cit.

I.

(25 cc. HYDROCHLORIC ACID ADDED.)

<i>t</i>	<i>x</i>	<i>ac</i>	<i>a'c</i>
0.....
10.....	2.20	0.0721	0.0804
20.....	3.10	0.0721	0.0844
25.....	3.35	0.0705	0.0845
35.....	3.70	0.0682	0.0856
50.....	3.95	0.0608	0.0802
70.....	4.20	0.0571	0.0816
100.....	4.40	0.0518	0.0822
130.....	4.50	0.0468	0.0796
$a = 5.25$		$a' = 4.935$	

II.

(20 cc. HYDROCHLORIC ACID ADDED.)

<i>t</i>	<i>x</i>	<i>ac</i>	<i>a'c</i>
0.....
10.....	1.60	0.0508	0.0521
21.....	2.40	0.0486	0.0544
50.....	3.25	0.0433	0.0520
70.....	3.55	0.0423	0.0534
95.....	3.80	0.0421	0.0571
$a = 4.75$		$a' = 4.50$	

III.

(15 cc. HYDROCHLORIC ACID ADDED.)

<i>t</i>	<i>x</i>	<i>ac</i>	<i>a'c</i>
0.....
10.....	1.40	0.0368	0.0426
20.....	2.15	0.0352	0.0424
30.....	2.60	0.0333	0.0416
40.....	2.95	0.0328	0.0426
50.....	3.25	0.0333	0.0454
70.....	3.50	0.0292	0.0423
80.....	3.65	0.0294	0.0442
90.....	3.75	0.0287	0.0448
$a = 5.2$		$a' = 4.68$	

IV.

(10 cc. HYDROCHLORIC ACID ADDED.)

t	x	ac	$a'c$
0.....
10.....	1.55	0.0298	0.0369
20.....	2.40	0.0276	0.0359
30.....	2.95	0.0259	0.0352
40.....	3.40	0.0254	0.0363
50.....	3.65	0.0236	0.0349
70.....	4.10	0.0216	0.0357
100.....	4.40	0.0187	0.0328
120.....	4.60	0.0178	0.0336
150.....	4.90	0.0177	0.0388
$a = 6.75$		$a' = 5.74$	

V.

(5 cc. HYDROCHLORIC ACID ADDED.)

t	x	ac	$a'c$
0.....
10.....	1.50	0.01911	0.0259
35.....	3.60	0.01789	0.0278
50.....	4.15	0.01596	0.0264
70.....	4.65	0.01413	0.0252
80.....	5.00	0.01437	0.0273
110.....	5.55	0.01327	0.0284
140.....	6.00	0.01279
170.....	6.35	0.01245
$a = 9.35$		$a' = 7.29$	

VI.

(NO HYDROCHLORIC ACID ADDED.)

t	x	ac	$a'c$
0.....
10.....	0.93	0.00921	0.0172
20.....	1.58	0.00836	0.0166
40.....	2.43	0.00706	0.0156
60.....	2.93	0.00603	0.0144
80.....	3.43	0.00564	0.0147
100.....	3.96	0.00560	0.0167
120.....	4.33	0.00539	0.0183
140.....	4.73	0.00536
190.....	5.23	0.00475
250.....	6.00	0.00477
320.....	6.33	0.00421
$a = 11.03$		$a' = 6.33$	

The above tables show that $a'c$ calculated by this means is much more nearly constant than ac , and that the variation between the values of $a'c$ is such as would be produced by experimental error. In the first four tables $a'c$ is calculated for all of the experimental values and is as nearly constant as can be expected with the exception of the last value in each table, where the experimental determination is subject to a large error. In the tables V and VI $a'c$ is not calculated for the final values, for in these cases the hydrolysis has been but slightly depressed by the addition of hydrochloric acid, and therefore the assumption that it is constant throughout the reaction, leads to a greater error than in the cases where the hydrolysis is not so great in amount. In these two cases, however, a fairly good constant can be calculated for the most important range of the tables.

A comparison of the values of ac and $a'c$ in the six tables shows conclusively that the hydrolysis has a very important, and calculable, effect on the constant. The fact that the error in ac continuously increases with the diminishing concentration of the hydrochloric acid leads to the same conclusion.

CORNELL UNIVERSITY,
December, 1894.

ON THE INFLUENCE OF MAGNETISM ON CHEMICAL ACTION.¹

BY F. A. WOLFF, JR.

Although the influence of magnetism on chemical action has been the subject of numerous investigations, the conclusions drawn by the various experimenters who have dealt with this problem are in many instances contradictory.

In the following brief résumé, the earlier investigations may be passed over, as they really did not bring to light any positive evidence one way or the other. In some cases a repetition of the experiments has even failed to verify the results recorded. Those made by Robert Hunt belong to this class, as Prof. Remsen has been unable to reproduce any of Hunt's results.

¹ From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1893.

In 1881 Prof. Remsen¹ discovered the remarkable influence exerted by a magnet on the deposition of copper, from one of its solutions, on an iron plate. In Prof. Remsen's own words: "When copper is deposited from a solution of copper sulphate on a plate of iron placed on the poles of a magnet, it is arranged in ridges around the poles in directions which are at right angles to the lines of force and consequently coincident with the lines marking the equipotential surfaces. Furthermore, the outlines of the poles of the magnet are always sharply defined on the plate as along these lines a portion of the iron of greater or less width is left unacted upon." The appearance of the plate is shown in Fig. 1.

This experiment redirected attention to the subject and Messrs. Nichols and Franklin² were the next to conduct experiments in this field.

They found that "passive" iron loses its passivity when brought into a magnetic field; also that when two iron electrodes, only one of which is magnetized, are dipped into a solution capable of acting upon them chemically, an electric current is established in the solution from the magnetized to the unmagnetized electrode.

Prof. Rowland and Bell³ were the first to observe the opposite effect. Experiments were made by them with iron, cobalt, and nickel electrodes in 30 different electrolytes; the electrodes were of different shapes, one sharply pointed and the other blunt, so that, when placed in a uniform magnetic field, they would become unequally magnetized. In all the cases examined they detected the existence of a current from the less strongly to the more strongly magnetized electrode, indicating that the latter was being protected. As Prof. Rowland has pointed out, the protection should be greatest where the rate of variation of the square of the magnetic force is a maximum.

Somewhat similar experiments were made by Andrews⁴ and Gross,⁵ who, however, obtained results analogous to those of Nichols and Franklin.

Loeb⁶ has approached the subject from a different direction, by determining the rate of oxidation of a ferrous salt and

¹ This Journal, **3**, 157; Science, **1**, 36. ² Am. J. Sci., **31**, 272; **34**, 419; **35**, 290.

³ Phil. Mag., **26**, 105.

⁴ Proc. Roy. Soc., **44**, 152; **46**, 176. ⁵ Sitzungsber. d. Wien. Akad., **112**, 1373.

⁶ This Journal, **13**, 145.

also the rate of reduction of a ferric salt, both within and outside of a magnetic field. No effect was detected in either case.

Lately, Andrews¹ has published another contribution to this subject, in which he shows that the rate of deposition of copper on iron bars, placed in a solution of copper sulphate, is accelerated by magnetizing them.

Last year in this laboratory, Mr. Geo. O. Squier² resumed the investigations of Rowland and Bell. His principal conclusions may be summarized as follows :

1st. When a pointed and a plane electrode of iron are placed between the poles of an electro-magnet in a solution capable of chemically acting on them, on first making the field, a current of small magnitude is always observed in such a direction as to indicate that the point is being protected from the action of the reagent.

2nd. That this current is momentary and is soon reversed in direction, if aqueous solutions be employed, and can often only be detected when bodily motion of the reagent is prevented by decreasing its fluidity with gelatin or some similar substance.

3rd. That this reversal is due to the concentration of the iron salts formed in the reaction, around the more strongly magnetized parts of the electrodes, and is *not* due to any *direct* influence exerted by the magnet.

Thus the directly opposite results obtained by Rowland and Bell were reconciled with those of Nichols and Franklin, Andrews, and Gross.

While this work was still in progress Mr. Squier and the writer undertook a joint investigation of the subject, under the direction of Prof. Rowland, to whom they are indebted for many valuable suggestions, from the point of view of Prof. Remsen's experiments. This seemed all the more promising since the "protective" effect as detected by the galvanometer was so very small, while in these experiments the effect was so very striking. The first part of this paper is therefore a joint production, but the writer was forced to pursue the investigation alone, owing to Mr. Squier's inability to continue the work in consequence of his professional duties.

¹ Proc. Roy. Soc., 52, 114.

² Phil. Mag., 35, 473.

The Rotations in the Liquid.

The original experiments of Prof. Remsen were first carefully repeated. Next to the absence of deposit over the outlines of the pole and the deposition in ridges, the phenomena which are most striking when a solution of copper sulphate is poured on an iron plate placed in a magnetic field, are the rotations in the liquid. In the course of a large number of experiments, using pole-pieces and plates of various forms, it was soon found that the rotations in the solution were connected with variations in the degree of magnetization of the plates and could, therefore, be made as complicated as possible by simply varying the form of the pole-piece. In one experiment the positions of minute iron screws, connecting the parts of the electro-magnet used, were indicated by rapid rotation of the liquid on the plate immediately above. In general, iron placed beneath the plate in any position produced local rotations in the liquid above.

That these rotations are electro-magnetic is quite evident. As was shown by Squier, when iron is attacked in a magnetic field, electric currents are established from the less strongly to the more strongly magnetized parts. This effect, being quite minute, is soon overpowered by secondary effects (the accumulation of the iron salts in the strongest parts of the field) which gives rise to currents in the opposite direction, and to these the rotations seem principally to be due. If the iron is not completely covered by a copper-deposit, local voltaic currents must also exist, and these, on account of the non-uniformity of the field, would, by its action, produce a resultant motion of the liquid. It would be quite difficult to take into account all of the effects when, besides, the viscosity of the solution introduces additional complication.

The simplest rotations observed were obtained when a pointed pole-piece was used. With circular plates there was only one rotation which was uniformly dextro above a north pole and levo above a south pole. These may be explained by the action of the field on the current from the part immediately above the pole-piece to adjoining parts of the plate.

With cylindrical pole-pieces the effects are more complicated as three distinct rotations may be observed. Above a north pole

the phenomena are as follows: The outlines of the pole are clearly marked by the absence of deposit. Inside this ring the rotation is dextro, and the deposit comparatively uniform. Directly over the ring and for some distance beyond, the rotation is levo and quite rapid. With larger plates a third rotation, dextro, of smaller angular velocity than the one over the outlines of the pole is seen. Whether this third rotation depends on *local* voltaic currents has not been determined.

That the main rotations are due to the concentration effects is shown by introducing with a pipette a few drops of a solution of ferric chloride above the center of a plate covered with water and placed on the pole of a magnet. The outlines of a pole are marked by a yellow ring due to the solution of ferric chloride which has been drawn up to it and the rotations begin immediately.

On pouring over the plate, dilute nitric acid, containing in solution the lower oxides of nitrogen, instead of copper sulphate, the outlines of the pole appear almost immediately as a dark ring due to the interaction of the ferrous salt formed in the reaction and the oxides of nitrogen.

Distribution of the Deposit.

It has been suggested that the absence of deposit over the outlines of the pole and the deposition in ridges is *directly* due to the magnetized condition of the metal. Let us, however, inquire how far the distribution of the deposit *could* be the result of the currents in the liquid and the concentration of the iron salts formed during the reaction, in the strongest parts of the field.

1st. Over the outlines of the pole there is no deposit.

The continual accumulation of iron salts in this region would certainly tend to decrease the amount of copper deposited there, and, moreover, the currents which originate there and proceed outward and inward *from* the "protected region" to other parts of the plate are accompanied by a corresponding amount of electrolysis. A certain quantity of iron goes into solution there, just as in other parts of the plate, but the equivalent amount of copper is deposited elsewhere on the plate, in excess of the amount being deposited on those parts by the normal action of the copper sulphate on the iron. These cur-

rents, since they go in the solution *from* the "protected region" to the other parts of the plate, should entirely prevent the deposition of copper over the outlines of the pole as the combination really constitutes a two-fluid cell, iron in contact with a solution of iron salts, and iron in contact with a solution of copper sulphate.

2nd. Directly outside the outlines of the pole the deposit is greatest.

This would, likewise, be a result of the electrolysis accompanying the currents from the "protected region" since the electromotive force between the ridge and the outer regions of the plate is practically constant, and since the magnetization at the ridge is immensely greater than that of the outer portions of the plate, the current to any particular portion, and, therefore, the accompanying electrolysis, is inversely proportional to the distance of that portion from the protected ridge, (that is, to the resistance). Hence, the deposit is thickest immediately adjoining the "protected ridge" marking the outlines of the pole. The deposit on the inside of the "protected region" also shows some indication of this action, but to a very much smaller degree, as one might expect since the degree of magnetization of these parts is more comparable with that over the outlines of the pole.

It is, therefore, quite probable that the absence of deposit over the outlines of the pole is not due to any *direct* influence of magnetism on chemical action, as has heretofore been supposed.

The question that still remained was, why is the deposit broken up in ridges?

On the Deposition in Ridges.

A number of possible explanations of this curious phenomenon suggest themselves.

1st. That the deposition in ridges is *directly* due to the magnetized condition of the iron.

2nd. That it is due to the presence of the voltaic currents, to which the absence of deposit over the outlines of the pole has been attributed.

3d. That it is produced by the mechanical flow of the solution over the plate.

A number of reasons point to the improbability of the first

hypothesis, as will be pointed out later. The second hypothesis was therefore the first to be tested.

Voltaic Currents.

Since the existence of an electric current arising from concentration of the iron salts formed during the reaction about the outlines of the pole accounted so well for the absence of deposit and the gradation of the deposit, it was thought that the deposition in ridges might also, in some way, be connected with it. Accordingly, an attempt was made to produce ridges by means of an extraneous current, within the region in which the deposit is practically uniform.

A pointed zinc rod was brought in contact with the center of an iron plate on the pole of a magnet and a solution of copper sulphate poured on as before. On examination, the deposit within the outlines of the pole was found to be arranged in spirals radiating from the point where the zinc rod touched the plate. Over a north pole the spirals were turned to the left, and on reversing the current in the electromagnet the spirals were turned in the opposite direction.

This curious phenomenon was all the more perplexing since it seemed to indicate that magnetism, at least in this special case, is *not* the direct cause of the deposition in ridges.

Prof. Rowland¹ has pointed out that, in consequence of the "Hall effect" the lines of flow of a current proceeding to or from a center in a thin metallic plate, placed in a magnetic field at right angles to the lines of force, would become spirals instead of radii. If, therefore, copper *should* be deposited in ridges along the lines of flow of a current in an iron plate on which is poured a solution of copper sulphate, this would furnish a possible explanation of the deposition in spirals. This supposition was accordingly tested. Since the "Hall effect" is opposite, in the case of nickel and iron, the spiral ridges, if formed, should from this cause turn in opposite direction when iron is replaced by nickel. It was found that mercury and platinum when deposited from their solutions on nickel, in a magnetic field, are not deposited in ridges, although the outlines of the pole are marked by the absence of deposit. Experiments along these lines gave, consequently, no definite results.

¹ Phil. Mag., 10, 301.

Experiments were next made on the deposition of copper on iron plates through which currents were flowing, both inside and outside the magnetic field. In the latter case it was found that the presence of a current did not destroy the uniformity of deposit until the strength of the current was sufficient to magnetize the plate to an appreciable extent. With a current of 150 amperes the copper was deposited in ridges along the lines of flow of the current. Small currents in an iron plate placed in a magnetic field did not seem to affect the form of deposit in the least, except when, as in the case of the zinc rod, a uniform motion in the solution was produced. This will be referred to below.

From these experiments the conclusion may be drawn that the deposition in ridges is not *directly* due to the voltaic currents existing in the solution or in the plate.

Bodily Motion of the Liquid.

That there is any effect due to the bodily motion of the liquid over the plate seemed at first improbable, for within the outlines of the pole where there is considerable rotation the deposit is uniform, and, moreover, when the plate is divided by a partition through the center, the ridges in either compartment do not seem to be in the least affected by it, as they begin immediately at the partition.

When a solution of nitric acid (15 per cent.) is used instead of copper sulphate, the outlines of the pole are soon marked by a dark ring and apparently before the liquid is set in bodily motion, dark markings, similar in appearance to the ridges of copper, are seen all over the plate. On pouring off the nitric acid the plate is found to be differently eaten away in different parts. The whole surface outside the protected ring is seen covered with circular markings, just as when copper is deposited on iron under the same circumstances.

To determine whether strains in the iron, which *do* exist in plates not uniformly magnetized, would produce any deposition in ridges when subjected to the action of copper sulphate, oblong rectangular strips of the metal were bent into circular arcs, and immersed in a solution of copper sulphate. It was found that the copper was uniformly deposited on them if they were carefully lowered into the solution. If,

however, they were rapidly plunged into the liquid, *the copper was deposited in ridges along the lines of first flow of the solution across the plate.*

When the strips were plunged into the solution with their concave side downward and inclined to the horizontal, the ridge on the concave surface converged toward the part of the strip which was last to be covered by the solution. See Fig. 2.

Similar effects were obtained when the convex side was held downward, the ridges being in the direction of first flow. Even with the non-magnetic metals, zinc and tin, the same result was obtained.

Fig. 3 shows the appearance of the under side of an iron plate, immersed in an inclined position in a solution of copper sulphate. It will be seen that the copper has been deposited practically in parallel ridges, along which the solution of the iron salt formed under these conditions would rise. The yellow solution was actually observed to rise from the upper edge of the plate in narrow columns corresponding to these ridges.

In the next experiments a steady stream of a solution of copper sulphate was caused to flow over metal plates from a small orifice. The deposit was in ridges along the lines of flow of the solution, and the same effects were obtained when iron, zinc, and tin were used. Fig. 4 illustrates its action on a tin plate under these circumstances.

These experiments show that ridges can be formed without the aid of magnetism by a mere mechanical flow, although it is not self-evident what the true explanation of this phenomenon is. That it is *not* due to any surface impurities of the solution was shown by first covering the plate with water and then allowing the solution to flow in beneath the surface of the water. As in the other cases, the copper was deposited in ridges along the lines of the flow. The spiral ridges obtained with the zinc rod were now readily accounted for, as, on closer inspection, solid particles suspended in the liquid were found to move spirally inward toward the point where the zinc rod and the iron plate were in contact.

Direct Effect of Magnetism.

There are quite a number of reasons which speak against the supposition that the deposition in ridges is due to the direct effect of magnetism on chemical action :

1st. There can hardly be any discontinuity of the magnetization of an iron plate corresponding to the ridges formed when a solution of copper sulphate is poured over it.

2nd. Inside the protected region the deposit is uniform, while in this region ridges are easily produced by mechanical flow.

3rd. It has been suggested that wherever the action of the solution begins, a cavity is formed and that the adjoining parts (edges) would therefore be more strongly magnetized and hence, "protected" from the further reaction of the reagent.

But to explain the deposition in circular ridges, for example, when cylindrical pole pieces are used, it would be necessary to assume that the plate is first attacked by the reagent in circles.

4th. The initial irregularities of the plate would also be magnified if this were the controlling cause, and moreover, these are greater than any which might be produced in a short time by the action of the solution.

A number of experiments seem to indicate that the deposition in ridges in a magnetic field is due to the rotations produced by the interaction of the field and the electric currents existing in the solution, for when the conditions are so modified as to prevent any motion of the liquid in contact with the metal the ridges do not appear. This was done in the following two ways :

1st. Enough gelatin was added to a solution of copper sulphate to make it stiffen on cooling. When the warm solution was poured on an iron plate in a magnetic field no deposition in ridges could be observed.

The "protective" action as shown by the galvanometer, is, however, best exhibited under these circumstances.

2nd. Placing a piece of filter paper on an iron plate in a magnetic field and pouring over it a solution of copper sulphate produced a similar effect. Where the paper touched the metal no deposition of ridges was observed, but wherever it was wrinkled and not in contact with the plate, the ridges were quite marked.

If the true explanation of the ridges is mechanical, it ought to be possible to detect motion along the ridges and, unfortunately, this cannot always be done. When drops of a solution of copper sulphate are placed on an iron plate in a magnetic

field, the copper is deposited in ridges in the same direction as if the whole plate had been covered with the solution. At first there is considerable commotion in the drop but soon no motion can be detected with a magnifying glass. Therefore, if the deposition in ridges is mechanical, the lines of first flow of the solution in contact with the plate must be in the direction of the ridges afterwards formed. How such a motion could be set up is not quite clear, but that the prevention of motion is attended by an absence of ridges seems to show that they are causally related.

When copper is deposited on tin in a magnetic field a whirl is set up about the point where the deposition begins, and ridges begin to appear along the lines of flow of the liquid. As the action of the solution soon starts up in other parts of the plate these whirls interact and, as a result, the copper is deposited in ridges of the most varied patterns.

Whether the regular deposition in ridges in the case of iron is due to the fact that more points are simultaneously attacked by the solution and that these whirls produce a resultant motion in the direction in which the ridges afterwards appear, cannot be affirmed.

Conclusions.

The conclusions reached may be summarized as follows :

1st. That the *absence* of deposit over the outlines of the pole is *not* due to any *direct* influence of magnetism on chemical action.

2nd. That it is due to the accumulation of the iron salts formed in the reaction about those parts *and* to the electric currents therefrom arising.

3rd. The fact that the deposit is thickest immediately adjoining the protected region also finds its explanation in the electrolysis accompanying these currents.

4th. That the deposition in ridges is not due to any direct influence of magnetism on chemical action.

5th. That the deposition in ridges is not directly due to the voltaic currents in the liquid.

6th. That copper is deposited in ridges on both magnetic and non-magnetic metal when a solution of copper sulphate is allowed to flow over them and that the ridges are arranged along the lines of flow.

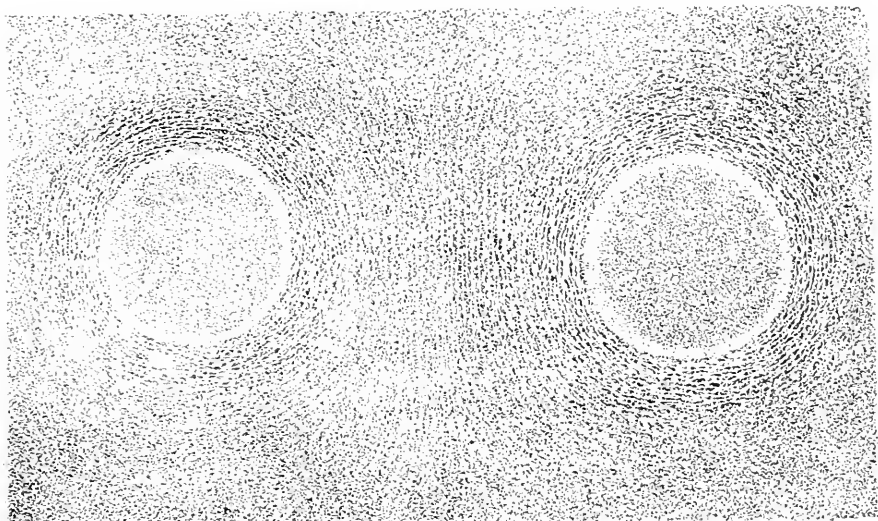


FIG. 1.

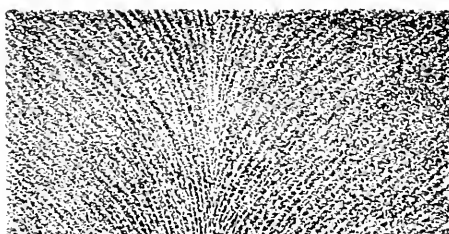


FIG. 2.

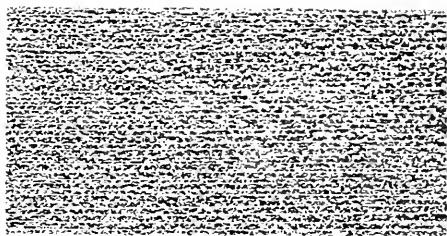


FIG. 3.

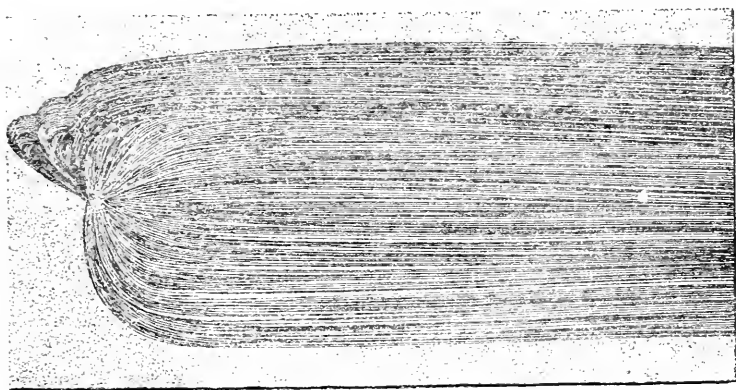


FIG. 4.

7th. That the deposition in ridges when copper is deposited on iron in a magnetic field may be due to similar action.

As will be seen, most of the effects described which have been attributed to the influence of magnetism on chemical action are due to secondary causes.

The "protective" effect first observed by Prof. Rowland is *now* the only incontestable evidence in favor of any direct effect.

As was stated above, this is very small indeed and probably finds its explanation in the increased work necessary to bring into solution the iron against the forces of attractions of the body of the metal when this is magnetized.

*Postscript.*¹

After the publication of the article in which the experiment which formed the starting point of this investigation was described, Prof. Remsen endeavored to find similar effects by replacing iron plates by plates of other metals and the copper sulphate solution by solutions of other metallic salts which are precipitated by the metal of the plates. Thus it was found that the action of copper and silver solutions on zinc and aluminium was apparently uninfluenced by placing the plates between the poles of an electro-magnet. This was also found to be the case in the action of copper solutions on tin and silver solutions on lead. In no case was the deposited metal arranged in well-defined ridges. These were also absent in the action of bismuth, silver, and mercury solutions on iron, platinum, and gold solutions (in *aqua regia*) on nickel. In all the experiments with iron and nickel, the outlines of the poles were well defined by a region of no deposit.

Prof. Remsen next experimented on the action of acids on metal strips placed in glass troughs on the upright poles of a horse-shoe magnet. Using iron and nickel strips and nitric acid, it was found that those parts of the strips directly over the poles were protected, though similar experiments with copper, zinc, and magnesium strips showed exactly the same effect.

The action of dilute hydrochloric and sulphuric acids on iron seemed to be fairly uniform but in these experiments the action was very slow.

¹ Since the publication of my first article on "Chemical Action in a Magnetic Field" (*loc. cit.*) I have done a good deal of work on the subject, but, in the main, the results have been disappointing. I have now placed my laboratory note-books at the disposal of Dr. Wolff with the request that he would make such use of them as seemed best, my direct interest in the matter having long since ceased. I. R.

The results obtained with the non-magnetic metals suggest that this phenomenon may, in part at least, be due to the cooling influences of the iron poles, and, moreover, this influence would be less marked the slower the action.

The interpretation of these experiments was still further complicated by the presence of the rotations observed in the liquid. These rotations are oppositely directed over the two poles.

A large number of *quantitative* experiments were also made on the action of acids on metal wires contained in test-tubes which were placed in the hollow core of a coil of wire through which an electric current was flowing, parallel experiments being always made in which the reaction took place in an exactly similar coil through which no current was flowing. Although it was found that copper wires were dissolved more rapidly within the coil carrying the current (due most probably to the increase of temperature arising from the heat generated by the current) iron wires were *less* rapidly dissolved, showing undoubtedly that the iron wires were protected in the magnetic field. It seems, however, that the protection observed is due not to the *direct* influence of magnetism, but to the accumulation of the iron salts formed in the reaction about the strongly magnetized ends of the wires. Accordingly, the protection should be less when the iron dissolves as ferrous salt than when it dissolves as ferric salt.

The results obtained with hydrochloric acid and with sulphuric acid were, therefore, not always uniform, as the protection was counteracted by the heating of the coil. This was also found to be true with nickel and nitric acid.

In a third set of experiments, the reaction was carried on in test-tubes between the poles of a large electro-magnet. The same general results were obtained as before, exceptions being readily accounted for by the variations in temperature, which would be produced by the proximity of the large iron pole-pieces and the heat generated in the coils of the electro-magnet, and subsequently conducted to the pole-pieces.

Hunt's Experiments.

Prof. Remsen then repeated the experiments of Robert Hunt.¹ but was unable to obtain any of the curious effects

¹ Mem. Geol. Sur. of Gt. Brit., 1, 433; Phil. Mag. (3rd series), 28, 4; and *Ibid.* (3rd series), 32, 252.

claimed to have been obtained. Some of these are described below.

1. *Deposition of Silver on Copper in a Magnetic Field.*—On pouring a weak solution of silver nitrate over a copper plate surrounded by an edging of wax and placed on the poles of a magnet, the precipitated silver, according to Hunt, arranges itself in curves radiating spirally in opposite directions from two points directly over the poles, and, if the reaction be allowed to continue, it will be found that “the acid of the silver salt has bitten deeply into the plate” in parts bearing definite relations to the position of the poles.

No effect of this kind could be obtained.

2. *Reduction of Silver Nitrate by Ferrous Sulphate.*—If solutions of these salts are mixed in a vessel placed on the poles of a magnet, according to Hunt, the reduced silver arranges itself in definite curves. Attempts made to verify this statement were also unsuccessful.

3. *Action of Mercury on Silver Solution in a Magnetic Field.*—The statement, that globules of mercury precipitate the silver in curves depending on the position of the poles, could not be verified.

4. *Action of Ferrous Sulphate on Silver Solution.*—Small tubes filled with a saturated solution of ferrous sulphate were inverted directly over the poles of a magnet, on which was placed a vessel containing a solution of silver nitrate. The precipitated silver was *not* arranged in “diamagnetic curves” (so called because they seemed to repel each other as they approached) as claimed by Hunt.

5. *Crystallization in a Magnetic Field.*—Experiments were made with solutions of ferrous sulphate and potassium ferrocyanide, but no influence of the field on the crystallization could be detected.

6. *Reduction of Ferric Sulphate in a Magnetic Field.*—Prof. Remsen next determined the rate at which an acidified solution of ferric sulphate is reduced by iron wires, both within and without a magnetic field. The differences observed were both positive and negative and did not exceed the experimental error.

Since then, Loeb¹ has studied both the rate of reduction

¹ This Journal, 13, 145.

and that of oxidation of iron salts by reducing and oxidizing solutions in a magnetic field, but he too reached the same conclusion as that arrived at by Prof. Remsen.

The experiments by Wartman¹ on electrolysis in a magnetic field were also repeated, copper being electrolyzed from a solution of the sulphate, and iron from a solution of ferric sulphate in potassium and ammonium oxalate. The results obtained were negative as were those of Wartman.

During the winter term (1893) the experiments of Robert Hunt² were again repeated by the writer. A few of the effects described could be reproduced, but these, it was found, could just as well be obtained without the aid of magnetism. In the first of Hunt's experiments described above, no such effect could be obtained, but even if it had been, this would have furnished no evidence of the influence of magnetism on chemical action, since there can be no possible connection between spiral ridges and the magnetic field which exists about the poles of a horse-shoe magnet. However, on pouring a weak solution of silver nitrate over a circular disk of copper fitted to the bottom of a crystallizing dish, it was noticed that the silver *was* deposited in spirals if the solution was poured in tangentially so as to give it a rotary motion. By the movement of detached silver particles it was made evident that the spirals marked the *lines of flow* of the liquid in contact with the plate, and consequently, when the solution was poured in from the opposite direction, the direction of the spirals, which become obliterated as the thickness of the silver deposit increases, is also reversed. It is possible that Hunt may have observed some such phenomenon, but it is difficult to see how it could have been produced in the rectangular vessels he used. No "bitten spaces" were ever observed, although silver solutions of various concentrations were used. In the experiment in which silver was precipitated from a solution of silver nitrate by a solution of ferrous sulphate, the spirals, in which the metal was deposited, were probably lines of flow of the solution, as the same effects can also be obtained without the aid of magnetism. In the modification of the foregoing experiment, in which a solution of

¹ Phil. Mag. (3rd series), 36, 30. ² Loc. cit.

ferrous sulphate was allowed to diffuse from inverted tubes into a solution of silver nitrate, the "diamagnetic curves" observed are merely lines of flow of the diffusing iron solution, as is readily shown by repeating the experiment without the aid of a magnet.

One of the experiments made by Prof. Remsen in connection with his repetition of Hunt's work, consisted in placing a crystal of mercuric chloride on a copper plate covered with water. It was found that the mercury was deposited on the the copper in "diamagnetic curves" (as Hunt would have called them) radiating out from the dissolving crystal, and, moreover, it was found that the same result was obtained both within and outside of a magnetic field. By *tilting the plate* it can easily be shown that the curves merely mark the lines of flow of the mercury solution formed by the dissolving crystal, for now the curves proceed in the direction in which the solution would flow if subjected only to the action of gravity.

The reason why a metal is precipitated in ridges along the lines of flow of a solution of one of its salts flowing over a plate of a second metal capable of precipitating it, has yet to be given. That the explanation is entirely mechanical is quite improbable, for the ridges are formed even when the velocity of the flow is comparatively small. In the course of the investigation the following explanation has suggested itself:

Consider, for example, the ridges formed by a solution of copper sulphate flowing over a tin plate. The action first begins at the source of flow and, wherever any copper is deposited, a solution of tin is formed. This is carried along by the motion of the copper sulphate solution, and, as the tin *must* go into solution at the surface of the plate, the liquid, directly in contact with the plate, becomes streaked with alternate streamers of copper solution, and tin solution. An electromotive force of considerable magnitude is thus established between adjacent portions of the surface, and necessarily gives rise to a large amount of electrolysis on account of the very low resistance of the local voltaic circuit established. More tin goes into solution in the streaks where it already exists; these become more pronounced, and thus assure the permanence of the ridges.

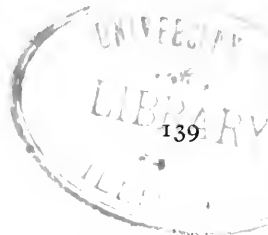
As was stated above, when an iron plate is placed in an

inclined position in a solution of copper sulphate, the copper sulphate on its *under* surface is found to be deposited in ridges. Streams of yellow iron solution, corresponding to the ridges, are observed to rise vertically from the rim of the plate in the clear blue copper solution above. In this case the solution in immediate contact with the under surface of the plate consists of alternate streamers of iron and copper solution, and the ridges are always in the direction in which gravity would cause the lighter iron solution to flow. Consequently the upper surface is only streaked when the plate is nearly vertical.

U. Behn¹ has lately shown that the ridges often observed in the Poggendorf silver-voltameter are produced by a flow resulting from the increased concentration of the silver solution about the anode (due to the unequal velocities of the ions). The cases examined by him were those in which the solution of a metal was *electrolyzed* between electrodes of the same metal, and the explanation of the phenomenon seems to be that the flow of the concentrated solution from the anode gives rise to a streaky condition of the solution, thus correspondingly changing its conductivity; and, therefore, the current-density on different parts of the cathode. Here too, as would be expected, the ridges mark the lines of flow of the concentrated silver solution over the surface of the cathode, and are, therefore, only observed when the cathode is directly beneath the anode.

The part which *magnetism* plays in the formation of ridges when a solution of copper sulphate is poured over an iron plate seems then to consist principally in giving rise to an unequal distribution of the iron salts formed in the reaction, to which most of the effects are *directly* attributable; in the production of electro-magnetic rotations in the solution; and in preventing the lighter iron solution from rising to the surface, thus assuring the permanence of electromotive differences once established.

¹ Wiedemann's *Annalen*, 51, 105. Ueber die streifenförmige Anordnung Galvanischer Niederschläge.



REVIEWS.

A TEXT-BOOK OF INORGANIC CHEMISTRY. G. S. NEWTH, F. S. C., F. C. S., Demonstrator in the Royal College of Science, London; Assistant Examiner in Chemistry, Science, and Art Department. London: Longmans, Green & Co., 1894. 667 pp.

In the preface Mr. Newth says: "In drawing up a systematic course of elementary chemical instruction based upon the periodic classification of the elements, a number of serious difficulties are encountered. I have endeavored to obviate many of these difficulties while still making the periodic system the foundation on which this little book is based by dividing the book into three parts. Part I contains a brief sketch of the fundamental principles and theories upon which the science of chemistry is built. Part II consists of the study of the four typical elements, hydrogen, oxygen, nitrogen, and carbon, and of their more important compounds. In Part III, the elements are treated systematically, according to the periodic classification."

Glancing at the table of contents, one finds that Part I contains fifteen chapters, covering 142 pages. These chapters contain all of the theoretical considerations which are scattered through the pages of most chemical text-books, and under the heads of general properties of liquids, electrolysis, solutions, osmotic pressure, thermo-chemistry, much that is usually omitted in elementary books.

The involuntary feeling of surprise at such a beginning, is tempered by noting a page entitled "Hints to Students," which follows the preface. The student is advised first carefully to read the first four chapters, pages 1 to 23, then to pass on to Part II, and to study the four typical elements and their compounds. During the time occupied in the study of these four elements, the student should "fairly master at least the first thirteen chapters of Part I." The first four chapters of Part I treat of chemical change, molecules, atoms, elements and compounds, chemical action, nomenclature, and other matters commonly taken up in the earlier chapters of text-books. On carefully examining these four chapters, however, the feeling of surprise returns. Whether definitions of mono and diatomic molecules, acidic and basic oxides, catalytic action, peracids, hypoacids, oxyacids, and thioacids, basicity of acids, can convey any meaning to the mind of a student who is not supposed to know anything of hydrogen or oxygen, is questionable.

Part 2 contains 150 pages. The present writer commends, to advanced students, a careful study of these chapters; closely condensed, thoughtful and suggestive they include a mass of

information found in few advanced text-books. One example may suffice. Among nitrogen compounds, hydrazine, hydrazine hydrate, hydrazoic acid, hydroxylamine, the ammoniumsulphonates and their hydroxylamine derivatives, the halogen compounds of nitrogen are briefly but lucidly discussed. Under the head of nitrogen iodide, the work of Courtois, Gladstone, and Lzuhay is clearly explained, though that of Mallet is not mentioned.

But this book is an elementary text-book, and the student has not yet taken up the study of the halogens. For him Part II seems at once too condensed and too full.

The "mastery" of the first thirteen chapters of Part I should now follow. Valency, atomicity, electrolysis, the constitution of hydrofluorsilicic acid and its analogues seem difficult to master before studying the properties of hydrochloric acid, or of any metals or bases.

The book is based on the periodic system. In the explanation of the system in the chapter devoted to it in Part I, and throughout part III, the author omits deductions from the system that would have been helpful to the student. For example, on page 338, the constitution of the oxyacids of chlorine is discussed. The structure of chloric acid $\text{Cl}-\text{O}-\text{O}-\text{O}-\text{H}$ is given, and the author continues: "It is possible that in some of these compounds the chlorine functions as a trivalent element, and that these compounds have a constitution similar to the oxides and oxyacids of nitrogen, thus, chloric acid,

$\text{H}-\text{O}-\text{Cl} \begin{array}{l} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$; nitric acid $\text{H}-\text{O}-\text{N} \begin{array}{l} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$." Later he says:

"Indeed, from a consideration of the salts of periodic acid, some chemists are in favor of assigning to iodine even a greater valency, and of regarding it as a heptad element in these compounds." In discussing the periodates, he speaks clearly of the many hypothetical periodic acids from which the salts known may be regarded as derived, but nowhere does he show how all of the oxyacids of the halogens may be simply classified and explained by the hypothesis of a halogen valence varying from 1 to 7, as suggested by the position of the halogens in the periodic system.

Again, the structure above given for nitric acid is the only one the present writer has found in the book. The author derives the phosphoric acids from pentavalent phosphorus, giving structural formulas, and says that the acids of arsenic and antimony correspond to those of phosphorus. Surely most chemists regard nitric acid as corresponding in structure with metaphosphoric acid, and think that the pentavalence of nitrogen in nitric acid follows from its position in the periodic system.

It would be captious to seek too closely for faults in a book which has much to recommend it, and while the present writer cannot think either the arrangement of the book, or its mass of condensed information suitable for an elementary text-book, these very qualities make it valuable as a handy reference book for the advanced student. Its thoroughness, its lucidity, the admirable way in which, for example, a subject so hackneyed as the methods of preparing oxygen, is made new and full of interest cannot be too highly praised. The many teachers who feel grateful to Mr. Newth for his admirable "Chemical Lecture Experiments" would look for these qualities in any book written by him, and will not lay this book aside without gratitude for many fresh suggestions on the most familiar subjects.

E. R.

NOTE.

The Relative Behavior of Chemically Prepared and of Atmospheric Nitrogen in the Liquid State.

The following abstract of a communication¹ by Professor James Dewar to the December meeting of the Chemical Society of London is of interest in connection with the subject of the discovery announced last summer by Lord Rayleigh and Professor Ramsay of a supposed new element in the air :

When gases, such as nitrogen, oxygen, or air, are liquefied in large quantities, the impurities found in the gases and taken up during the passage through the pumps gradually accumulate, and when the fluids are discharged into vacuum vessels at atmospheric pressure these separate in the solid state. If the solid matter is filtered off from liquid air and the fluid allowed to evaporate slowly from a vacuum vessel, then the last drops of liquid are almost pure oxygen; nitrogen gas containing 3 or 4 per cent. of oxygen when liquefied behaves exactly in the same way. It would appear, therefore, that no impurity of higher boiling-point than oxygen can be separated by ordinary fractional distillation of the liquid air, and if any other material is present it must evaporate along with the nitrogen. By the use of a special arrangement, small quantities of gases, in a pure and dry state, amounting to from 100 cc. to a few liters, may be examined in the liquid condition and the experiment repeated as often as desired with the same specimen of gas.

The simple apparatus exhibited, by means of which the condensing-point of a gas and afterwards the volatilizing rate

¹Before reading his paper, Professor Dewar exhibited a vacuum-jacketted globe containing about half a liter of liquid air, which had been kept for the previous thirty hours at the Royal Institution.

of the resulting liquid may be observed, may be succinctly described as follows:—A tube of small bore, somewhat drawn out at one extremity, is passed nearly to the bottom of a distillation flask and sealed into the neck. The outer portion of this tube is closed and bent twice at right angles, so that a closed limb is thus formed outside the vessel. The side tube of the flask is sealed after the pure, dry gas under examination has been introduced, together with phosphorus pentoxide, at a known pressure and temperature. The closed limb of the small bore tube is then cautiously introduced into a vacuum-jacketted tube containing liquid air or oxygen, so arranged that the vapor pressure on the liquid may be gradually lowered by means of an air pump, and the gas within the tube slowly reduced to the temperature of liquefaction. In this way it is easy to observe the point at which liquid begins to form from different samples of gas placed side by side, and afterwards, when the temperature of the liquid air-bath is allowed to rise, the point at which the last drops of the liquids resume the gaseous form. Nitrogen obtained from atmospheric air has been compared in this manner with nitrogen prepared from nitric oxide without any differences between them being detected. Atmospheric nitrogen which has been passed over heated magnesium showed, however, a marked difference as compared with gas which had not been so treated. Although its condensing-point was not far removed from that of the untreated material, as a matter of fact this point, as well as the volatilizing-point of the resulting liquid, was higher than before, that is to say, nitrogen which has been passed over heated magnesium becomes liquid a little before the original specimen, and the liquid evaporates rather more slowly and lasts longer when both substances are compared under precisely similar circumstances. Nitrogen, chemically prepared from nitric oxide, was likewise changed by passing it over heated magnesium, for after this operation it liquefied and evaporated at a rather higher temperature than previously.

It would, therefore, appear that, whilst atmospheric nitrogen does experience change when passed over heated magnesium, some effect is also produced on chemically prepared nitrogen; and, as far as these experiments have been carried, they reveal no very marked difference between the behavior of nitrogen from atmospheric air and nitrogen obtained from its compounds by chemical methods. It may be, however, that any concentrated impurity boils nearly at the same temperature as the original nitrogen, or that the amount present is so small that it does not liquefy at the temperature of -200° C. Considering that the flasks of 150 cc. capacity contained

the concentrated impurity of 10 liters of nitrogen, the partial pressure of small quantities of other matter ought to be very considerable, so that we might anticipate liquefaction at -200°C . At the lowest temperature reached, atmospheric nitrogen which had been passed once over magnesium gave clear, transparent crystals along with liquid, while the untreated nitrogen remained fluid. All the samples of nitrogen and oxygen properly purified, when liquefied in the above manner, are clear, transparent liquids, so that the solid matter which always separates when air or nitrogen or oxygen is liquefied on the large scale consists of impurities. If a manometer is attached to the flask containing the gas, and at the same time the condensing-tube is calibrated, the method of working gives quantitative results, since the pressure in the flask and the volume of liquid condensed can be simultaneously observed.

Further, if we use liquid oxygen as the cooling agent, we can observe the vapor pressures of two or more substances at the same temperature, and these pressures may be expressed in terms of the vapor pressure of oxygen. In this way all very volatile liquids would be comparable with oxygen as a standard.

It must be understood that these experiments are merely qualitative, and were not carried out with the view of separating any new substance from air or nitrogen. Their chief object is to observe the points of condensation and evaporation of gases liquefying between -180°C . and -200°C . at and below atmospheric pressure.

Small amounts of known impurities cause marked differences in the amount of liquid formed from the same volume of gas similarly treated. Thus, a trace of impurity, presumably hydrogen, in a sample of nitrogen subjected to liquefaction in the above manner only gave one-third the volume of liquid that a similar flask gave when filled with pure nitrogen. This is due to the concentration of the hydrogen or other non-liquefiable material in the narrow tube where liquefaction takes place.

This plan of working may be conveniently applied to testing whether the oxygen and nitrogen in air liquefy simultaneously. Such a question cannot be answered by liquefying air under pressure. If, however, two flasks, such as have been described, are taken, one filled with nitrogen at 0.79 of the atmospheric pressure, and the other with oxygen at 0.21 of the atmospheric pressure (the temperatures being equal), then, on cooling them side by side, the instant at which liquefaction takes place in the narrow condensing tubes can be observed. The oxygen always appears a few seconds before

the nitrogen, and remains after the latter has evaporated. The boiling-points of nitrogen and oxygen, under the respective pressures at which they exist in the atmosphere, are very close together.

In the discussion which followed this communication, the President, referring to experiments on the liquefaction of gases which he had recently witnessed in the Royal Institution Laboratory, said that the means of producing very low temperatures during long periods, now at Professor Dewar's disposal there, were marvellously complete, and important results ought, before long, to flow from their application.

It was useless to deny that special interest attached to the communication to which they had just listened, but, unfortunately, in the absence of Lord Rayleigh and Professor Ramsay, they were left in the position of having to play "Hamlet" with only the ghost present, and, under such circumstances, the play obviously could not be continued to a successful issue. Chemists were deeply interested by the statements relating to the discovery of a new constituent of the atmosphere, brought before the British Association at Oxford, but they awaited further information before making up their minds. They were in a very different position, however, since Friday last, when the President of the Royal Society, in his address, referred to this discovery as the greatest scientific event of the year. It was to be supposed that the President of the Royal Society had information at his disposal, not hitherto made public, which justified so definite a statement, and naturally chemists would impatiently await its disclosure. He ventured to say that Lord Rayleigh and Professor Ramsay now could not hope to keep so remarkable a discovery to themselves much longer. After having been told so much, chemists could not be expected to remain quiet under the imputation that they had been eyeless during a whole century, and they would undoubtedly inquire into the matter. Although no one would seek to take the discovery out of the hands of those who had announced it, chemists unquestionably had the right, not only to exercise entire freedom of judgment, but also to critically examine the statements which had been made. With regard to Professor Dewar's observations, which were such as could only be made with the aid of the low temperature appliances at his disposal at the Royal Institution, Professor Dewar would be the first to admit that they were of a qualitative character, and open to several interpretations; but they were certainly highly suggestive.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LXXXIV.—ON THE CUPRIAMMONIUM DOUBLE SALTS.

SECOND PAPER.¹

BY THEODORE WILLIAM RICHARDS AND ANDREW HENDERSON WHITRIDGE.

The continuation of the study of the cupriammonium double salts, begun in 1891,² has led to the preparation of the following new compounds:

- (1) $\text{Cu}(\text{NH}_3)_2\text{ClCHO}_2$.
- (2) $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.
- (3) $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_2$.
- (4) $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_3$.
- (5) $\text{Cu}(\text{NH}_3)_2\text{ClC}_3\text{H}_5\text{O}_3$.

(1) CUPRIAMMONIUM FORMICHLORIDE, $\text{Cu}(\text{NH}_3)_2\text{ClCHO}_2$.

The bromide corresponding to this chloride has been described already by Richards and Shaw. The chloride itself was

¹ Presented at a meeting of the American Academy of Arts and Sciences, held May 9, 1894.

² Theo. W. Richards: Ber. d. chem. Ges., **25**, 1492; T. W. Richards and H. G. Shaw: This Journal, **15**, 642; Proc. Am. Acad., **28**, 247.

obtained at the same time by these experimenters, but only in an impure state, and the present problem was to determine the conditions necessary for the preparation of the substance in a state of purity.

If any considerable amount of water is present in the materials, basic salts of copper are certain to be precipitated, and to contaminate the preparation. On the other hand, the slight solubility of cupric formiate and cupriammonium chloride in alcohol makes it difficult to avoid the admixture of these substances with the desired compound, if alcohol is used in the anhydrous condition.

The following procedure was found to be the most successful, but great care was needed to carry it out. 3 grams of crystallized cupric formiate were dissolved in just enough warm alcohol to effect solution, and 2 grams of ammoniac chloride were added to the mixture. The whole was then heated to boiling, and dry ammonia was passed in until a very slight excess was present. Upon cooling and evaporation in the air, fine blue prismatic crystals separated, which were fairly pure, as the analyses show. The salt resembles in its properties the formibromide, being permanent in dry air, but at once decomposed by water. In color it is a purer blue than the formibromide, having much less of the greenish tinge.

In the analysis of the compound the copper was determined electrolytically after the substance had been evaporated with sulphuric and nitric acids. The chlorine from a new portion was weighed as argentic chloride, and the ammonia was distilled after the addition of potash. The formic acid was determined by combustion.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{ClCHO}_2$.

I. 0.0862 gram substance gave on electrolysis 0.0305 gram Cu.

II. 0.0997 gram substance gave on electrolysis 0.0356 gram Cu.

III. 0.1258 gram substance yielded 0.0994 gram AgCl.

IV. 0.1285 gram substance yielded 0.1008 gram AgCl.

V. 0.1060 gram substance distilled with caustic potash required 11.75 cc. of a decinormal solution for neutralization.

VI. 0.0984 gram substance yielded on combustion 0.0241 gram CO_2 .

Analyses III and IV were made from different samples; hence, they prove the definiteness of the compound.

	I.	II.	III.	Found. IV.	V.	VI.	Aver- age.	Calculated for $\text{Cu}(\text{NH}_3)_3\text{ClCHO}_2$.
Cu	35.38	35.71	35.54	35.69
NH_3	18.91	18.91	19.15
Cl	19.54	19.40	19.47	19.90
CHO_2	25.05	25.05	25.26
							98.97	100.00

(2) AMMON-CUPRIAMMONIUM ACETOBROMIDE,
 $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.

This compound is formed readily when cupric bromide is dissolved in a mixture of alcohol and glacial acetic acid, and an excess of dry ammonia gas is passed into the solution. It is essential to have the solutions concentrated. For example, 2.5 grams of cupric bromide were shaken with 13 cc. of glacial acetic acid and 25 cc. of alcohol. Upon cooling, after the addition of the ammonia which raised the temperature of the solution, the desired substance separated out. If, when passing in the gas, a black precipitate ($\text{Cu}_3\text{Br}_6[\text{NH}_3]_{10}$) falls after the solution has become dark purple,¹ the supernatant liquid should be decanted before it is allowed to crystallize. The precipitate shows the presence of an excess of cupric bromide in proportion to the acetic acid.

Ammon-cupriammonium acetobromide had already been made by Richards and Shaw; but the analyses of the compound were so unsatisfactory that no account of the substance was given in their paper. This unsatisfactoriness was due, not to any difficulty in preparing the substance in a state of purity, as in the previous instance, but rather to the great difficulty of drying the substance enough without drying it too much. The extra molecule of ammonia and the molecule of water are held very loosely, mere exposure to the air allowing

¹ Richards and Shaw, *loc. cit.*

them to escape. Especially is this the case when the substance is placed over sulphuric acid. 0.1242 gram of material, which had been exposed thus until constant in weight, yielded 0.0331 gram, or 26.65 per cent. of copper upon electrolysis. This showed that the substance had lost practically all of its extra ammonia and water, for the theoretical per cent. of copper in $\text{Cu}(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$ is 26.87. The new salt consists of pearly flakes of a brilliant light blue color, somewhat less intense than that of the normal cupriammonium acetobromide. It is only very slightly soluble in alcohol, and is at once decomposed by water, a little of the copper going into solution. In properties and general appearance, it resembles the ammon-cupriammonium acetochloride prepared by Richards and Shaw, except that it is much less stable.

The acetic acid was determined by distillation with phosphoric acid, according to the well-known method of Fresenius. Hydrobromic and a trace of phosphoric acid which come over in the distillate were precipitated with argentic nitrate from the neutralized solution, the result being calculated as argentic bromide, since this is the greater part of the precipitate.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.

I. 0.3276 gram substance yielded 0.0774 gram Cu upon electrolysis.

II. 0.3902 gram substance yielded 0.0896 gram Cu upon electrolysis.

III. 0.3376 gram substance yielded 0.2365 gram AgBr.

IV. 0.2453 gram substance yielded 0.1732 gram AgBr.

V. 0.4214 gram substance yielded 0.2940 gram AgBr.

VI. 0.2600 gram substance distilled with caustic potash required 13.28 cc. of a decinormal acid solution for neutralization.

VII. 0.1528 gram substance distilled with caustic potash required 16.29 cc. of a decinormal solution for neutralization.

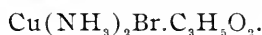
VIII. The distillate from a mixture of 0.1469 gram substance with phosphoric acid required 5.67 cc. of decinormal alkali for neutralization. Approximately corrected for alkalimetric equivalent of argentic phosphate and bromide obtained from distillate, this amount becomes 5.47 cc.

	I.	II.	Found. III.	IV.	V.
Cu	23.63	22.97
NH ₃
Br	29.81	30.04	29.68
C ₂ H ₃ O ₂
H ₂ O (diff.)

	VI.	Found. VII.	VIII.	Average.	Calculated for above formula.
Cu	23.30	23.40
NH ₃	18.20	18.19	18.19	18.84
Br	29.84	29.42
C ₂ H ₃ O ₂	22.35	22.35	21.72
H ₂ O (diff.)	6.32	6.62
				<hr/> 100.00	<hr/> 100.00

It is evident that most of the substance analyzed had lost some of its ammonia and water. A few other determinations were made of substance just prepared and not dried at all, in order to be sure that the atomic ratio of the ammonia to the copper was not greater than 3:1. This point was proved beyond a doubt.

(3) CUPRIAMMONIUM PROPIONOBROMIDE,



10 grams of ammoniac propionate, made by neutralizing propionic acid with ammonia gas and allowing the solution to evaporate over caustic potash, were mixed with 2 grams of cupric bromide, and dissolved in about 50 cc. of absolute alcohol. Dry ammonia gas was passed into the solution, and on standing, a precipitate of cupriammonium bromide



came down. 4.5 cc. of strong propionic acid were added to dissolve the precipitate, and more ammonia gas was added. Again the same crystals appeared, showing that the tendency to form this substance was much more decided than the tendency to form the substance desired. Since the addition of more propionic acid did not help the matter, 1.5 grams of precipitated cupric oxide were added, and the whole was warmed until most of the powder had dissolved. After filtration and evaporation in the air, prismatic crystals of a very strong blue

color were deposited, proving to be the substance sought. The crystals were washed with alcohol, and dried in the air, in which they are permanent. 0.5750 gram of the substance was found to displace 0.2197 gram of toluol having a specific gravity of 0.8619; hence, the specific gravity of cupriammonium propionobromide is 2.255. The other properties resemble so closely those of the acetic compound that it is not worth while to detail them.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_2$.

I. 0.1017 gram substance gave on electrolysis 0.0262 gram Cu.

II. 0.1061 gram substance gave on electrolysis 0.0270 gram Cu.

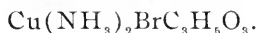
III. 0.0825 gram substance yielded 0.0624 gram Ag.Br.

IV. 0.0788 gram substance distilled with caustic potash, required 6.19 cc. of decinormal acid for neutralization.

V. 0.1109 gram substance yielded 0.0588 gram CO_2 upon combustion.

	I.	II.	Found. III.	IV.	V.	Average.	Calculated for above formula.
Cu	25.76	25.45	25.60	25.37
NH_3	13.40	13.40	13.61
Br	32.18	32.18	31.90
$\text{C}_3\text{H}_5\text{O}_2$	29.31	29.31	29.12
						100.49	100.00

(4) CUPRIAMMONIUM LACTOBROMIDE,



This compound is easily obtained by dissolving syrupy lactic acid and about a third of its weight of cupric bromide in alcohol, and then passing dry ammonia gas into the solution. Basic salts of copper do not form readily here, but if an insufficiency of lactic acid is added, $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ will crystallize out. The crystals are of a strong light blue color, with a faint tinge of purple; they may be obtained of great size. They are permanent in the air, and at once decomposed by water. 2.6377 grams of the substance were found to displace 1.0334 grams of toluol, indicating a specific gravity of 2.20.

For analysis the salt was washed twice with alcohol, and pressed between filter paper.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{BrC}_3\text{H}_5\text{O}_3$.

I. 0.1742 gram substance gave on electrolysis 0.0418 gram Cu.

II. 0.1108 gram substance yielded 0.0786 gram AgBr.

III. 0.1916 gram substance yielded 0.1360 gram AgBr.

IV. 0.0850 gram substance required on distillation 6.25 cc. of decinormal acid solution for neutralization.

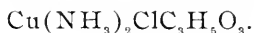
V. 0.0987 gram substance required 7.38 cc. of decinormal acid.

VI. 0.1634 gram substance yielded on combustion 0.0819 gram CO_2 .

Analyses II and III were made from different samples of the substance.

	I.	II.	Found.		V.	VI.	Average.	Calculated for above formula.
			III.	IV.				
Cu	23.99	23.99	23.85
NH_3	12.56	12.84	12.70	12.79
Br	30.19	30.20	30.19	29.99
$\text{C}_3\text{H}_5\text{O}_3$	33.79	33.79	33.37
							100.67	100.00

(5) CUPRIAMMONIUM LACTOCHLORIDE,



4 grams of cupric lactate were dissolved in strong alcohol, and when the solution was boiling, 2 grams of ammoniac chloride were added. Through this solution, perfectly dry ammonia gas was passed until slightly in excess. Upon filtering and evaporating the solution, fine crystals of cupriammonium lactochloride were deposited. A similar method would have answered in the case of the bromide. These crystals are of a somewhat lighter blue color than the lactobromide, but otherwise their properties are similar. Because of this similarity, determinations of the chlorine and copper were considered enough to identify the compound.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{ClC}_3\text{H}_5\text{O}_3$.

I. 0.1751 gram substance gave on electrolysis 0.0496 gram Cu.

II. 0.1341 gram substance gave on electrolysis 0.0382 gram Cu.

III. 0.1314 gram substance gave on electrolysis 0.0378 gram Cu.

IV. 0.1025 gram substance yielded 0.0659 gram AgCl.

V. 0.1015 gram substance yielded 0.0656 gram AgCl.

	I.	II.	Found. III.	IV.	V.	Average.	Calculated for above formula.
Cu	28.83	28.49	28.76	28.52	28.64
Cl	15.93	15.98	15.95	15.96

Attempts were made to make similar compounds of butyric acid without success. Various different proportions, suggested by those required in the previous preparations, were tried with uniform failure, and the attempts were finally discontinued.

It was also hoped that such compounds as $\text{Cu}(\text{NH}_3)_2\text{ClNO}_3$ and $\text{Cu}(\text{NH}_3)_2\text{NO}_3 \cdot \text{C}_2\text{H}_3\text{O}_2$ might be formed. The results of a great many experiments showed that under ordinary conditions nothing but $\text{Cu}(\text{NH}_3)_2\text{Cl}_2$, or $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ can be obtained. Further attempts to combine cupriammonium sulphate with cupriammonium acetate were also unsuccessful; so that in these directions the field seems to be limited. All of these facts, as well as the relative properties of those compounds which have been prepared, may be of some use in the future when the structure of the cupriammonium compounds comes under consideration. Work upon the subject, as well as upon similar investigation of products containing amines instead of ammonia, is being continued here.

CAMBRIDGE, MASS., *September*, 1894.

LXXXV.—THE COMPOSITION OF ATHENIAN POTTERY.

BY THEODORE WILLIAM RICHARDS.

At the request of Mr. Edward Robinson, of the Boston Museum of Fine Arts, several analyses of ancient Athenian pottery were recently made at this laboratory. While the interest of these analyses was mainly archeological, turning upon the question of the identity of the source of these remains with that of others found in other cities,¹ a brief

¹ Catalogue of Greek, Etruscan, and Roman vases, Museum of Fine Arts, Boston, page 35.

statement of the results may not be uninteresting to those working upon the subject of clays in general.

The color of the broken pottery was usually pale red; the black or transparent glaze upon the outside surfaces was always very carefully scraped off before the material was pulverized. For much of the work, I am indebted to Messrs. J. A. Widtsoe and Howard Lyon; in every case the name of the analyst is recorded below.

Sample 1.—Fragment of a vase. Platinum vessels were used almost exclusively in the execution of this analysis. 1.0745 grams of the finely powdered specimen yielded 0.6015 gram of silica, 0.2771 gram of mixed ferric and aluminic oxides, 0.0651 gram of calcic oxide, and 0.1373 gram of magnesian pyrophosphate. The iron required for oxidation, 11.60 cc. of a permanganate solution, of which 1 cc. corresponded to 0.0056 gram of iron. The small amount of residue from the silica, after treatment with hydrofluoric acid, was fused with acid potassic sulphate and added to the filtrate containing the remainder of the bases.

2.184 grams of the powder yielded 0.1317 gram of mixed sodic and potassic chlorides, and these yielded 0.3173 gram of potassic chloroplatinate.

0.8843 gram of clay lost 0.0062 gram at 105° and 0.0293 gram more at a red heat.

Results, Analysis I, [Richards].

Silicic oxide.....	56.00	per cent.
Aluminic oxide.....	17.15	"
Ferric oxide.....	8.64	"
Baric oxide.....	trace	
Calcic oxide.....	6.05	"
Magnesian oxide.....	4.63	"
Potassic oxide.....	2.80	"
Sodic oxide	0.84	"
Water at 105°	0.70	"
Water at red heat.....	3.31	"
	<hr/>	
	100.12	"

The other partial analyses given below were made with the intention of finding out if there were any great variations in the relative proportions of the different oxides in different samples. They were made in glass vessels; hence, in each case the total result is probably too high.

Sample 2.—Handle of a vase. Specific gravity = 2.193.

	Widtsoe.	Lyon.	Average.
Silica.....	54.24	54.01	54.12
Residue from silica...	0.58	0.30	0.44
Alumina.....	17.99	18.45	18.22
Ferric oxide.....	9.88	10.04	9.96
Lime.....	6.03	6.04	6.04
Magnesia.....	5.46	5.49	5.48

Sample 3.—Fragment of a jar.

	Widtsoe.	Lyon.	Average.
Silica.....	56.57	56.65	56.61
Residue from silica...	1.36	0.78	1.08
Alumina.....	18.11	18.01	18.06
Ferric oxide.....	8.12	8.62	8.40
Lime.....	5.05	5.17	5.11
Magnesia.....	4.40	4.40
Potash.....	2.98	2.98

Sample 4.—Fragments of a vase; and

Sample 5.—Neck of a vase :

	4. Widtsoe.	5. Widtsoe.
Silica ..	56.79	57.08
Residue from silica....	0.37	0.57
Alumina.....	14.82	16.80
Ferric oxide.....	9.03	8.23
Lime.....	5.95	4.85
Magnesia.....	4.86	5.09

The variations in the relative amounts are singularly small, the range being not nearly so large as that given by Brougniart, in his “*Traité des Arts Céramiques.*” Hence, it is probable that all of these specimens, which were picked up in the city of Athens itself, were the product of a local pottery.

CAMBRIDGE, MASS., *January*, 1895.

A REDETERMINATION OF THE ATOMIC WEIGHT OF YTTRIUM.

BY HARRY C. JONES.

The separation of those elements which occur together in such minerals as gadolinite, samarskite, etc., has always been a matter of considerable difficulty, due largely to the close agreement in the properties of the elements in question.

As a consequence of this, what were at one time supposed to be elementary substances, have since been shown to be mixtures of two and in some cases of a group of elements, whose compounds were so closely allied in properties as to escape the chemical methods of separation which had been employed.

Spectrum analysis, which has been so fruitful in other fields, has been of value here in showing that the substances which were supposed to be individuals were really mixtures. The atomic weights of these rarer elements have been determined from time to time by analyzing their compounds which were thought to be pure, with the result that widely different values have been found for the same element, by different experimenters using different preparations of what was regarded as the same substance. This is well shown in the case of yttrium, whose atomic weight as determined varies from about 105 to 89.1 This is not surprising, since it seems now to be pretty well established that only in one or two cases has even a fairly pure yttrium compound been obtained and used.

This but serves to show that, while the atomic weight of most of the more common elements can be regarded as known to within comparatively narrow limits, the atomic weight of some of the rarer elements may not yet have been correctly determined to within several units.

We need better methods for separating these mixtures that we may obtain purer compounds from which the atomic weights of the elements can be determined, and any step which will aid us in this direction cannot be without some interest and value.

A method more satisfactory than any hitherto employed for separating yttrium from many of the constituents which occur with it seems to have been found by Professor Rowland in connection with his study of the spectra of the rarer elements. Although an account of this method has already been published,¹ yet it is desirable to cite here that part of it which has to do directly with the separation of yttrium by the use of potassium ferrocyanide.

“This is the most useful process and easily separates the

¹ Johns Hopkins Univ. Circular, 112, 73; reprinted in Chem. News, 70, 68.

element (yttrium) pure and free from all others. To obtain pure yttrium from the mineral gadolinite, fergusonite, or samarskite: First obtain the crude mixed earths in the usual manner; then separate the cerium group as usual until the absorption bands of neodymium no longer appear. For the complete separation without loss this must be done several times, as much of the yttrium group is carried down with the first precipitate. * * * * *

"The separation of the yttrium from the other elements is effected by precipitating the latter from a weak acid solution by potassium ferrocyanide. For this purpose the filtrate, after separating the cerium group, can be used at once by slightly acidulating with nitric acid, diluting, and adding a weak solution of potassium ferrocyanide. No precipitate should appear at once, but on standing for an hour or so some will come down. Add more potassium ferrocyanide and repeat until the filtrate no longer shows the bands of so-called erbium. After this it is best to precipitate with oxalic acid or potassium oxalate, and ignite the precipitate so as to get the earth. Dissolve this in nitric acid and add only water enough to make a very concentrated syrupy solution. Place in a beaker at least three inches in diameter and examine with a spectroscope of low power for absorption bands. Probably the bands of neodymium and "erbium" will appear. Separate the first by sodium sulphate as usual, and the last by potassium ferrocyanide from an acid solution as above. The filtrate will then contain the pure yttrium, whose calcined oxalate will be pure white without trace of yellow. After separation of iron, calcium, and, possibly, manganese, the earth will be a pure element, as far as I can tell, spectroscopically. However, like Zr, Fe, and many other substances, the addition of Na or K to the electric arc, while obtaining the spectrum, will change the intensity of certain lines of the spectrum, while others are unchanged. If this is considered as evidence of the existence of two elements, then the same evidence will apply to Fe and Zr. The reason for believing that the substance thus found is an element is based on the fact that its spectrum remains unaltered in all minerals and after all chemical operations that I have been able to devise.

Furthermore, I believe that the new process is not only more easy than any other but also that it has given a single element for the first time. * * * The yield will, of course, depend on the amount of purity required. From the earths of gadolinite about one-tenth of quite pure yttrium can be obtained and about one-twentieth of very pure.

"I have determined spectroscopically that when, by the above process, the absorption band of "erbium" at last disappears from 3 inches of strong solution, all the other elements have also disappeared.

"By taking the first precipitate several times by potassium ferrocyanide from an acid solution, a mixture of many elements is obtained which contains much of that element to which the so-called "erbium" band is due. By dissolving a weighed quantity of this mixture in nitric acid and water, and examining the band spectrum, I have determined the limit when the band can no longer be seen. Thus I have proved that when the band vanishes from 3 inches of concentrated syrupy solution of yttrium there cannot exist in it more than $\frac{1}{2}$ per cent. of the mixed element as compared with the yttrium, and there is probably less.

"I have not found potassium ferrocyanide useful in the further separation of the elements, but only in separating out α (yttrium) from the others.

"When the neodymium band has disappeared by use of sodium sulphate, all the other elements of the cerium group have disappeared. The element thorium is sometimes present in the crude earths, but disappears after a while from the purified earths. The conditions for its disappearance I have not determined."

A specimen of yttrium oxide, purified by the above-described process, was furnished me by Prof. Rowland for the purpose of determining the atomic weight of yttrium. While the yttria was free from all other rare elements with certainty to within $\frac{1}{2}$ per cent., and probably to within much less, yet the spectrum showed that it might contain traces of calcium, magnesium, iron, and manganese. To remove the traces of these impurities, if present in the yttria, the latter was dissolved in strong nitric acid and the excess of acid evaporated

off on the water-bath. The slightly acid solution was then diluted with a large volume of water and the yttrium precipitated from the hot solution by ammonia from which all carbonate had been removed, as yttrium hydroxide. The hydroxide precipitated in this manner is somewhat gelatinous but is more easily filtered and washed than when precipitated from a cold solution. To wash the yttrium hydroxide thoroughly was a somewhat tedious process. The precipitate was allowed to settle and the supernatant liquid decanted as completely as possible. The precipitate was then treated again with hot water, well shaken, and allowed to settle. The water was again decanted and the process repeated many times until the precipitate seemed to have been well washed. A small quantity of the hydroxide was then brought on the filter and washed many times with boiling water; this was removed, another small quantity filtered off and washed, and this continued until all of the yttrium hydroxide had been finally washed in this manner. By this process any calcium or magnesium would have been separated from the yttrium.

The yttrium hydroxide was then dissolved in nitric acid and the yttrium precipitated from the acid solution by oxalic acid, which had been repeatedly crystallized from cold water, as yttrium oxalate. The crystalline oxalate was brought on the filter also in small quantities, washed well with hot water, and dried in an air-bath. The dry oxalate was ignited in a platinum crucible over the blast-lamp until the pure oxide remained. In this way any iron or manganese would have been separated from the yttrium.

The yttria thus obtained from the oxalate was pure white when heated over the blast-lamp for a short time. After prolonged heating at a very high temperature it seemed to me to acquire a faint yellow tint. Another observer declared, however, that he was unable to detect a trace of yellow.

The oxide which had been heated for a short time as well as that which had been heated more vigorously, was tested for calcium, magnesium, iron, and manganese by chemical tests, but these failed to show the presence of either of the above-named elements in the yttria.

About 6 grams of yttria were thus obtained free from all the

more common elements and containing as a maximum impurity $\frac{1}{2}$ per cent. of the rarer oxides. This is the yttria which was used in the following determinations.

The platinum crucible in which the yttrium oxalate was decomposed to the oxide and which was used throughout the work, was carefully cleaned, and finally, in order to remove any iron which might distill out into the yttria, was heated for a long time in the vapors of ammonium chloride.

All weighings of the platinum crucible, either when empty or when containing the yttrium compound, were made with the crucible placed within a ground-glass stoppered weighing-tube for protection from the atmospheric moisture. This was necessitated by the hygroscopic character of the anhydrous yttrium sulphate. The crucible with its contents was placed in the weighing-tube, while still warm and the tube closed. Further cooling took place in a desiccator over calcium chloride. The stopper was removed from the tube for an instant just before weighing, to insure equalization of the air pressure. All the weighings were reduced to a vacuum standard. A long-armed Becker balance was used and the accuracy of the weights insured by previous comparisons.

I. Conversion of the Oxide into the Sulphate.

The platinum crucible was heated over the blast-lamp to constant weight. The desired amount of yttria, which had been already well ignited, was placed in the crucible and heated again for a short time over the blast-lamp. It was then weighed, reheated, and reweighed. In no case was any loss in weight detected, due to the second heating.

The oxide in the platinum crucible was then treated with sulphuric acid of the concentration 1 acid to about 3 of water, and placed in an ordinary air-bath and warmed gently until most of the excess of sulphuric acid had evaporated. The sulphate usually began to crystallize from the solution before all the oxide was dissolved. For this reason large amounts of oxide could not be employed in any single determination, since, with large quantities, one could not be certain that all the oxide had been transformed into sulphate. In one or two of the determinations made there was some doubt on this

point, but, that the oxide was completely converted into sulphate in all of the determinations, the results of which are given below, is shown by the fact that the sulphate was found in each case to be entirely soluble in water. The crucible containing the yttrium sulphate, a little free sulphuric acid, and, probably, some acid sulphate was then placed in an air-bath of such a form that it could be more highly heated than before. This bath consisted of a cylinder of copper about 12 cm. high and 10 cm. in diameter, into the opposite sides of which two large holes had been cut and covered with plates of mica. This enabled one to see through the bath at all times. A thick plate of copper was riveted on to the bottom and allowed to project on all sides about an inch beyond the cylinder, to prevent reducing gases from the flame from entering the bath and coming in contact with the yttrium compound. The top of the bath was covered with a plate of iron and this in turn with a sheet of asbestos. The platinum crucible was supported on a porcelain triangle about an inch from the bottom of the bath. The bath was heated by two triple burners to a little above the boiling-point of sulphuric acid. This removed all free sulphuric acid and decomposed any acid sulphate which might have been present, as was shown by testing a solution of the sulphate in water with methylorange, with which acid sulphates give an acid reaction. The sulphate was heated in this bath to constant weight. That there was no decomposition of the sulphate into basic sulphate was indicated by the two facts, that constant weight was quickly established and that the resulting sulphate was entirely soluble in water.

When the anhydrous sulphate was brought in contact with water the greater part of the salt dissolved at once, while a small portion took up water and passed over into the crystalline salt with water of crystallization. The crystalline sulphate is less soluble than the anhydrous, but on heating the solution every trace of it dissolved.

A few determinations by this method were lost by accident. In one or two cases where larger amounts of oxide were employed and not a very great excess of sulphuric acid, the sulphate, when dissolved in water, was found to contain

traces of oxide. Below are the results of the ten determinations which were successfully carried to completion :

	Y_2O_3 .	$Y_2(SO_4)_3$.	$3(SO_3)$.	$\left. \begin{array}{l} \{ O = 16. \\ \{ S = 32.06. \} \end{array} \right\}$ At. wt. yttrium.
I.....	0.2415	0.4984	0.2569	88.89
II.....	0.4112	0.8485	0.4373	88.92
III.....	0.2238	0.4617	0.2379	88.97
IV.....	0.3334	0.6879	0.3545	88.94
V.....	0.3408	0.7033	0.3625	88.90
VI.....	0.3418	0.7049	0.3631	89.05
VII.....	0.2810	0.5798	0.2988	88.94
VIII....	0.3781	0.7803	0.4022	88.89
IX.....	0.4379	0.9032	0.4653	89.02
X.....	0.4798	0.9901	0.5103	88.91
Total ...	3.4693	7.1581	3.6888	
Average.....				88.94

The mean value of the ten determinations is 88.94, with a maximum value of 89.05, and a minimum value of 88.89. The atomic weight of yttrium, calculated from the total oxide used, 3.4693 grams and the total sulphate found, 7.1581 grams, is 88.94. All of the above and following calculations are based on oxygen = 16 and sulphur = 32.06 ; $SO_3 = 80.06$.

II. *Conversion of the Sulphate into Oxide.*

Yttrium sulphate was prepared by dissolving the oxide in dilute sulphuric acid and evaporating the solution to a small volume on the water-bath, when the sulphate crystallized out. The mother-liquor was then poured off and the sulphate dried by pressing between filter paper. The desired amount of the sulphate was placed in the platinum crucible, which had been heated over the blast-lamp to constant weight, and itself dried to constant weight in the cylindrical air-bath previously described, at a temperature a little above the boiling-point of sulphuric acid. The weighed sulphate was then decomposed to the oxide in the platinum crucible over the blast-lamp. During the latter part of the heating the lid was removed from the crucible and the oxide heated in direct contact with the air.

The heating was continued until the oxide had attained a constant weight and the oxide was tested in every case for the presence of sulphate. When constant weight was reached

under the conditions employed, every trace of sulphate had been decomposed to oxide.

To test the reliability of this method, a weighed amount of yttrium oxide was converted into sulphate by the method first described and then this sulphate decomposed to oxide by the method just described. If the method of decomposition of the sulphate was trustworthy then the same amount of yttrium oxide should have resulted from the decomposition of the sulphate as was originally used. Two such tests were made and in both cases the amount of oxide obtained from the sulphate agreed with the amount originally used to within a tenth of a milligram.

Below are the results of the ten determinations by this method, which were finished satisfactorily. Here also an occasional determination was lost by accident.

	$Y_2(SO_4)_3$.	Y_2O_3 .	$3(SO_3)$.	$\left. \begin{array}{l} O=16. \\ S=32.06. \end{array} \right\}$ At. wt. yttrium.
I	0.5906	0.2862	0.3044	88.91
II	0.4918	0.2383	0.2535	88.89
III.....	0.5579	0.2705	0.2874	89.03
IV	0.6430	0.3117	0.3313	88.99
V	0.6953	0.3369	0.3584	88.89
VI	1.4192	0.6880	0.7312	88.99
VII.....	0.8307	0.4027	0.4280	88.99
VIII....	0.7980	0.3869	0.4111	89.02
IX	0.8538	0.4139	0.4399	88.99
X	1.1890	0.5763	0.6127	88.96
Total....	8.0693	3.9114	4.1579	
Average.....				88.97

The mean atomic weight from the ten determinations is 88.97, the highest value found being 89.03, the lowest 88.89. The atomic weight of yttrium calculated from the total sulphate, 8.0693 grams and the total oxide 3.9114 grams, is 88.97.

The agreement between the two series of determinations is satisfactory and the atomic weight of yttrium, as determined from the oxide which I employed, is about 88.95.

Historical Sketch.

To show how widely the results of the different determinations of the atomic weight of yttrium, which have been

made, differ from one another, I give the following brief sketch :

The earliest determination was made by Berzelius¹ in 1818. From his analysis of the carbonate, Ostwald² has calculated the atomic weight $Y = 105$. Meyer and Seubert³, from Berzelius' analysis of the sulphate, have calculated the atomic weight $Y = 96.77$. ($O = 16$.)

From the analysis of the sulphate made by Popp,⁴ (1864), Ostwald has calculated the atomic weight $Y = 102.13$. From Popp's determination of yttrium in the sulphate by precipitation as oxalate and weighing as oxide, Meyer and Seubert have found the atomic weight $Y = 101.90$. ($O = 16$.)

From the determinations of water in the sulphate, made by Delafontaine⁵ (1865), Meyer and Seubert have found the atomic weight $Y = 97.86$. ($O = 16$.) From his determinations of yttrium in the sulphate, they calculate $Y = 96.64$. ($O = 16$.)

Bahr and Bunsen⁶ (1866) dissolved yttrium oxide in sulphuric acid, evaporated on the water-bath, and gradually heated above the boiling-point of sulphuric acid. From the results, Meyer and Seubert give $Y = 92.80$. ($O = 16$.) Pure oxide was transformed into basic nitrate, and in this way was found $Y = 92.48$.

The above determinations are now only of historic interest, since, in the light of more recent discoveries, it is almost certain that in each case mixtures of yttrium with other rare earths, some of which were known and others not suspected, were employed.

Cleve and Höglund⁷ (1873) seem to have had the purest material up to their time. By converting the oxide into the sulphate, they found $Y = 89.58$. ($O = 16$, $S = 32.06$.)

Cleve⁸ (1883) converted as pure yttria as could be obtained into the nitrate and repeatedly fractioned by means of oxalic

¹ Schweigg. J., **22**, 336; **16**, 422. Pogg. Ann., **8**, 186.

² Lehrbuch, zweite Auflage, Bd. I, 122.

³ Atomgewichte der Elemente.

⁴ Ann. Chem. (Liebig), **131**, 191.

⁵ Ann. Chem. (Liebig), **134**, 109.

⁶ Ann. Chem. (Liebig), **137**, 21.

⁷ Bihang till. Vet. Afs. Handl., 1873, I, III, No. 8.

⁸ Bul. Société Chimique, **39**, 120.

acid. Finally he obtained a small quantity of yttria whose molecular weight remained constant. This was separated by means of oxalic acid into four fractions, each of which gave a sulphate containing about the same quantity of yttria. 23.2091 grams of the sulphate gave 11.2568 grams of the oxide. From this follows $Y = 89.1$. ($O = 16$, $S = 32.06$.)

There seems to be no doubt that Cleve's yttria was the purest hitherto employed and his determination has, up to the present, been justly regarded as nearest to the true atomic weight of the element.

The value which I have found is about 0.15 of a unit lower than that of Cleve, which argues for a corresponding increase in purity in my material over that of Cleve's, since the impurities commonly present have a higher atomic weight than yttrium. The impurity in the oxide which I used, which from spectrum analysis cannot exceed $\frac{1}{2}$ per cent., and is probably less according to Rowland, is very likely a remnant of the "erbium" group which was not completely separated by the potassium ferrocyanide. The true atomic weight of the element yttrium is then, in all probability, a little lower than 88.95, the value found from the yttria which I employed.

Crookes¹ has recently raised the question as to whether the atomic weight of the yttrium obtained by Rowland had been determined. The work described in this paper, which was carried out before Crookes' communication was seen, will, it is hoped, answer that question satisfactorily.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIV.,
December, 1894.

Contributions from the Chemical Laboratory of the University of Michigan.

SEPARATION OF NICKEL AND IRON.

BY E. D. CAMPBELL AND W. H. ANDREWS.

In the separation of two elements that are at all closely related chemically, such as nickel and iron, it is desirable, if possible, first to precipitate the element sought for, as it will be accompanied by only a small amount of the second element. In, by far, the greater number of methods heretofore

¹Chem. News, 70, 81.

proposed for separating nickel and iron, the iron is precipitated first, carrying with it more or less nickel. The amount of nickel precipitated with the iron is variable, depending upon the composition of the precipitate, the relative proportions of the two elements, concentration of the solution, and various other conditions. The recovery of this small amount of nickel, especially if much iron be present, is usually a long, tedious process. A number of processes have been proposed in which nickel is precipitated first, the principal object in these methods being to avoid the necessity of having to handle a large, bulky precipitate of iron.

Classen¹ precipitates nickel as double potassium nickel oxalate in acetic acid solution, the iron being kept in solution as double oxalate.

Thomas Moore² first converts both iron and nickel into double cyanides with potassium cyanide; then precipitates nickelic hydroxide by means of potassium hydroxide and bromine, leaving iron in solution as potassium ferricyanide. G. A. Leroy³ deposits electrolytically both iron and nickel from an ammoniacal solution of their sulphates containing ammonium citrate, then by reversing the current redissolves, and reprecipitates nickel, leaving ferric hydroxide in suspension. G. Vortmann⁴ recommends the direct electrolysis of the ammoniacal sulphate of nickel in the presence of suspended ferric hydroxide.

The authors have worked out the following method which, if carefully followed, will be found to give accurate and easy separation of nickel from iron: To the mixed metals in nitric acid solution, with from 20–25 cc. excess of nitric acid is added sodium pyrophosphate dissolved in warm water. The amount of sodium pyrophosphate required should be in the proportion of about 13 grams to each gram of the metal present, which will be a slight excess over what is necessary to form the double pyrophosphate. After the addition of the sodium pyrophosphate to the ferric and nickelous nitrates contained in a medium-sized Erlenmeyer flask, the

¹ Ztschr. anal. Chem., 1879, p. 189–193.

² Chem. News, 56, 3, 1887.

³ Chem. News, 63, 194, 1891.

⁴ Monatsh, 14, 537, 1893.

white ferric pyrophosphate first precipitated is brought into solution by cautiously adding a clear, moderately concentrated solution of sodium carbonate, agitating thoroughly until the precipitate just dissolves and the solution attains a dull, olive-green color. An excess of sodium carbonate must be carefully avoided, as the subsequent precipitation of nickel will be incomplete if this is not done.

The solution of the double pyrophosphates of nickel and iron is filtered through asbestos into a half-liter flask and nickel precipitated as brick-red nickelous xanthate by the addition to the cold solution of 2 grams of potassium xanthate, freshly dissolved in a little water. The flask is then stoppered and shaken at frequent intervals for ten minutes when the precipitation will be complete. It is then filtered through asbestos and the nickelous xanthate immediately washed with fresh 1-per cent. solution of potassium xanthate. This precipitate is dissolved off the filter with a small amount of freshly diluted (1:1) fuming nitric acid. After adding 2 cc. of sulphuric acid, previously diluted with a little water, the solution is boiled down until nitric acid is completely expelled and sulphuric anhydride fumes begin to rise. The nickelous sulphate thus obtained is dissolved in a small amount of water and the iron accompanying it precipitated by the addition of a slight excess of ammonium hydroxide. The ferric hydroxide is filtered out, redissolved with a small amount of dilute sulphuric acid, reprecipitated with ammonium hydroxide, and filtered, the second filtrate being added to the first. Even when the original amount of iron is large, the ferric hydroxide taken from the nickel solution seldom exceeds 0.003 gram. The ammoniacal solution of nickel sulphate is then transferred to a large platinum dish capable of holding about 200 cc.; 3 grams of disodic-hydric phosphate dissolved in water is added, together with 25 cc. of strong ammonium hydroxide and the nickel deposited electrolytically by passing through it, a current of about 0.14 amperes per 100 sq. cm. area of the dish for twelve hours. Or, the nickel in the slightly ammoniacal filtrate from the precipitate of ferric hydroxide may be determined volumetrically by means of a standard solution of potassium cyanide, adding as an indicator, silver nitrate followed

by potassium iodide, the suspended silver iodide giving an opalescence to the solution which does not clear up until all the nickel has been completely converted into potassium-nickel double cyanide.

In making test separations by the above methods, varying amounts of nickel wire of known composition were weighed out and dissolved by an assistant who then delivered them as samples strictly unknown to the operator until the analysis was completed. In this way any prejudice on the part of the operator due to a previous knowledge of the amount of nickel present was avoided, and the method given a strictly fair test. The accuracy of the recovery may be judged from the following table in which the amount of iron added, of nickel taken and recovered, gain or loss, and method for the final determination, are given :

Iron added.	Nickel taken.	Nickel recovered.	Gain or loss.	Method.
Grams.	Grams.	Grams.	Grams.	
0.2105	0.08892	0.08910	+0.00018	Electrolysis.
1.0000	0.03430	0.03435	+0.00005	"
1.0041	0.05298	0.05345	+0.00047	"
1.0043	0.10824	0.10825	+0.00001	"
2.0043	0.02690	0.02740	+0.00050	"
Grams.	Grams.	Grams.	Grams.	
1.0010	0.00100	0.00089	-0.00011	Volumetric.
1.0086	0.06578	0.06532	-0.00046	"
1.0066	0.07582	0.07583	+0.00001	"
1.0057	0.08017	0.08050	+0.00033	"
1.0071	0.09389	0.09381	-0.00008	"

On account of the satisfactory results obtained on the separation of nickel from iron with potassium xanthate, further research is being made in the use of that reagent as a precipitant.

ANN ARBOR, MICH., December, 1894.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.¹

BY WOLCOTT GIBBS, M. D., *Rumford Professor Emeritus in Harvard University.*
[Continued from p. 91, Vol. 17.]

Auramin Pyrophosphates.

When a solution of double chloride of gold and sodium,

¹ Presented at a meeting of the American Academy of Arts and Sciences, held August 1, 1894.

AuCl_4Na , is made as nearly neutral as possible and then boiled with sodic pyrophosphate, $\text{P}_2\text{O}_5\text{Na}_4$, a very pale yellow solution is formed, which contains the auro-sodic salt discovered by Persoz, the formula of which we should now write $\text{P}_2\text{O}_5\text{Au}^{\text{III}}\text{Na}$. The solution of this salt gives with ammonia a white precipitate which quickly becomes yellow and crystalline. With argentic nitrate it gives a pale yellow flocky crystalline precipitate, which is very insoluble and does not blacken readily in the light. With mercurous nitrate it gives a greenish gray flocky crystalline precipitate. A nearly white curdy precipitate is formed with sulphate of luteo-cobalt; none with sulphate of croceo-cobalt. With $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ gold is reduced.

The crystalline precipitate formed by ammonia in the auro-sodic pyrophosphate solution was well washed, dried at 150° , and analyzed.

0.9665 gram gave 0.6756 gram $\text{Au} = 78.44$ per cent. Au_2O_3 .
 0.9031 gram gave 0.7003 gram $\text{Au} = 78.34$ per cent. Au_2O_3 .
 0.9665 gram gave 0.1621 gram $\text{P}_2\text{O}_5\text{Mg}_2 = 10.73$ per cent. P_2O_5 .
 1.0031 grams gave 0.1703 gram $\text{P}_2\text{O}_5\text{Mg}_2 = 10.86$ per cent. P_2O_5 .
 0.7375 gram gave 0.02286 gram $\text{NH}_3 = 3.10$ per cent.
 0.7691 gram lost at 150°C. , 0.0420 gram $\text{H}_2\text{O} = 5.46$ per cent.

The analyses lead to the formula



which requires

		Calculated.		Found.
14 Au_2O_3	6178	78.34	78.44	78.34
6 P_2O_5	852	10.80	10.73	10.86
14 NH_3	238	3.02		3.10
3 Na_2O	186	2.36		2.26 (diff.)
24 H_2O	432	5.48		5.46
	<hr/> 7886	<hr/> 100.00		

The analysis is due to Dr. Morris Loeb, who assisted me in this part of my work most efficiently.

The salt does not explode at low temperatures, but on heating to a little above 170°C. , a violent explosion takes place. This shows clearly that part at least of the gold is in the form of an auramin, or compound with ammonia.

The auramin pyrophosphate of sodium, on boiling with baric chloride, gives a yellow crystalline salt; with mercuric chloride, a fine pale yellow crystalline salt which becomes very distinct on boiling.

When the auramin salt is boiled with mercurous nitrate, some mercury is reduced to metal, and at the same time very characteristic white prismatic crystals are formed. Chlorhydric acid does not sensibly dissolve the pyrophosphate, but changes it to a pale yellow flocky crystalline body. Chloride of luteo-cobalt gives, on boiling, an orange crystalline salt.

When the crystalline yellow or dull orange baric salt is well washed with hot water and then filtered off, the colorless filtrate, on evaporation, gives with sodic hydrate a very distinct reaction for ammonia. Part of the ammonia in the salt must, therefore, have been in the form of ammonia, unless we admit that the auramin is decomposed under the circumstances. When treated with a cold solution of argentic nitrate, reaction sets in at once, and a fine yellow flocky crystalline salt is formed; but no trace of ammonia is obtained from the filtrate after washing the salt with cold water and separating the excess of silver. Both the barium and silver salts were partially analyzed.

The barium salt was analyzed by Mr. G. W. Patterson:

0.6472 gram gave 0.1015 gram $\text{BaSO}_4 = 10.30$ per cent. BaO .

0.6472 gram gave 0.1426 gram $\text{P}_2\text{O}_5\text{Mg}_2 = 14.09$ per cent. P_2O_5 .

0.6472 gram gave 0.3900 gram $\text{Au} = 67.63$ per cent.

Here the ratios are $9 \text{Au}_2\text{O}_3 : 6 \text{P}_2\text{O}_5 : 4 \text{BaO}$.

In the silver salt (Patterson):

0.7718 gram gave 0.0915 gram $\text{AgCl} = 9.58$ per cent. Ag_2O .

0.7718 gram gave 0.4470 gram $\text{Au} = 64.98$ per cent.

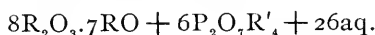
0.7718 gram gave 0.1584 gram $\text{P}_2\text{O}_5\text{Mg}_2 = 13.13$ per cent. P_2O_5 .

The ratios are approximately $16 \text{Au}_2\text{O}_3 : 10 \text{P}_2\text{O}_5 : 5 \text{Ag}_2\text{O}$.

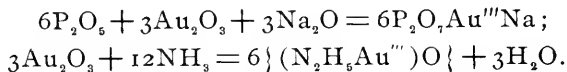
The analyses of the barium and silver salts are at least sufficient to show that no simple double decomposition takes place in either case. The formula which I have given for the gold salt is to be regarded as purely empirical, and does not explain the explosive character of the salt. No compounds

falling under the general expression $\text{Au}_2(\text{NH}_3)_n\text{O}_3$ are at present known. Dumas and Raschig give to fulminating gold the formula $\text{NH}_2.\text{Au}'''\text{.NH}$, which may be written $\text{N}_2\text{H}_3\text{Au}'''$. This is equivalent to 2NH_3 ; the corresponding ammonium must be $\text{N}_2\text{H}_5\text{Au}'''$, and the oxide of this $(\text{N}_2\text{H}_5\text{Au}''')\text{O}$. If we assume that this oxide is present in the auramin pyrophosphate which I have described, we may write the formula

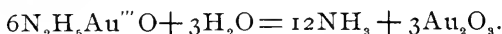
$8\text{Au}_2\text{O}_3.6\text{P}_2\text{O}_7.\text{Au}'''\text{Na}.6\{(\text{N}_2\text{H}_5\text{Au}''')\text{O}\}(\text{NH}_4)_2\text{O}.2\text{H}_2\text{O}+24\text{aq.}$, which is reducible to the type



As regards the deduction of the formula from the analyses, it may be worth while to give also the equations



In the determination of the ammonia by boiling with KHO or NaHO, we have



Auro-pyrophosphomolybdates.

When a solution of chloro-aurate of sodium, AuCl_4Na , is mixed with one of pyrophosphomolybdate of sodium, a dull orange-colored fine-grained crystalline precipitate is thrown down, which is almost certainly an auro-pyrophosphomolybdate of sodium. When a solution of auro-pyrophosphate of sodium, $\text{P}_2\text{O}_7.\text{AuNa}$, is boiled for some time with 14:6 molybdate of ammonium, a pale buff-colored crystalline precipitate is formed, which is slightly soluble in boiling water, giving, however, only a turbid liquid. After washing with cold water this precipitate was dried *in pleno* over sulphuric acid. Of this salt:

0.5581 gram lost by ignition with WO_3Na_2 0.0841 gram $\text{H}_2\text{O}+\text{NH}_3+\text{O}=15.07$ per cent.

$\left\{ \begin{array}{l} 0.8123 \text{ gram gave } 0.3489 \text{ gram Au} = 42.94 \text{ per cent.} = 48.18 \\ \text{per cent. Au}_2\text{O}_3. \\ 0.8123 \text{ gram gave } 0.0837 \text{ gram P}_2\text{O}_7.\text{Mg}_2 = 6.59 \text{ per cent.} \\ \text{P}_2\text{O}_5. \end{array} \right.$

0.6133 gram gave 0.2615 gram Au = 42.13 per cent. = 47.85 per cent.

0.2746 gram gave 0.01558 gram NH_3 = 5.65 per cent. NH_3 .

0.4774 gram lost by ignition with WO_4Na_2 0.0744 gram = 15.58 per cent.

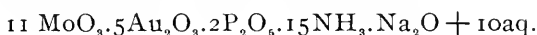
In this last analysis the salt had probably absorbed a little water. The same is true for the next:

0.6133 gram gave 0.0624 gram $\text{P}_2\text{O}_5\text{Mg}_2$ = 6.51 per cent.

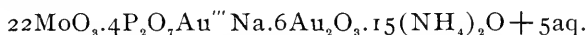
If we calculate the analyses for an anhydrous salt, we find :

		Calculated.	Found.	
11 MoO_3	1584	36.07		
5 Au_2O_3	2206	50.25	50.29	50.27
2 P_2O_5	284	6.46	6.87	6.83
15 NH_3	255	5.81		5.89
Na_2O	62	1.41		
	<hr/>	<hr/>		
	4391	100.00		

In the hydrated salt the ratios are nearly



The formula requires 3.93 per cent. of water. The mean of the water in the two analyses is 4.18. It is to be borne in mind that the salt could not be recrystallized, and was probably not absolutely pure. The salt does not explode on heating, but merely "puffs." Hot dilute chlorhydric acid readily dissolves it. Ammonia-water does not sensibly dissolve it, but gives an orange-colored substance which may be the corresponding auramin compound. The formula may be written provisionally



More extended investigations are necessary to fix the formulas of this and analogous compounds. Analysis by Mr. G. W. Patterson.

Auramin-pyrophosphomolybdates.

When the orange-colored flocky precipitate formed by adding ammonia to auro-pyrophosphate of sodium is boiled for some time with 14 : 6 ammonic molybdate, and the whole allowed to stand with the supernatant liquid, a pale yellowish crystalline salt is formed. After thorough washing with cold

water, the salt was dried on bibulous paper and *in pleno* over sulphuric acid. For analysis it was boiled for a short time with a mixture of chlorhydric and sulphurous acids. The phosphoric acid was determined in the filtrate from the gold by magnesia-mixture, in the manner which I have pointed out in treating of the analysis of the phosphomolybdates.¹ The filtrate from the ammonio-magnesian phosphate, after adding $(\text{NH}_4)_2\text{S}$, was evaporated, filtered to separate free sulphur, and then treated with cold dilute chlorhydric acid. The precipitated MoS_3 was filtered on a Gooch filter, washed, dried at 106°C. , then washed several times with carbon disulphide, dried, and weighed. Ammonia was determined by boiling with sodic hydrate and titration.

(1) 0.3969 gram gave 0.0217 gram $\text{NH}_3 = 5.47$ per cent.

(2) 0.5733 gram gave 0.3612 gram $\text{Au} = 70.68$ per cent.

(3) 0.5733 gram gave 0.1168 gram $\text{P}_2\text{O}_5, \text{Mg}_2 = 13.03$ per cent.
 P_2O_5 .

(4) 0.5733 gram gave 0.0426 gram $\text{MoS}_3 = 5.57$ per cent.
 MoO_3 .

(5) 0.3499 gram lost on ignition with WO_3, Na_2 0.0703 gram
 $= 20.09$ per cent.

The salt explodes on heating, but not violently. There appears to have been a slight loss on heating with sodic tungstate, and I have accordingly calculated the water by difference, all the other constituents having been determined directly. The analyses correspond to the formula



Analysis by Mr. G. W. Patterson.

		Calculated.	Found.
12 Au_2O_3	5297	70.54	70.68
3 MoO_3	432	5.75	5.57
7 P_2O_5	994	13.23	13.03
24 NH_3	408	5.44	5.47
21 H_2O	378	5.04	5.25
	<hr/>	<hr/>	
	7509	100.00	

Here, as in the cases of the other gold compounds, part of the ammonia is present as ammoniac oxide and part is directly

combined with gold ; but the proportions remain to be determined. The careful study of this class of compounds appears likely to lead to very interesting results. I have classed them only provisionally with complex acids.

As it may not be possible for me to return to the subject,¹ I will here give the results of some preliminary work, which will at least serve as starting-points for further investigation.

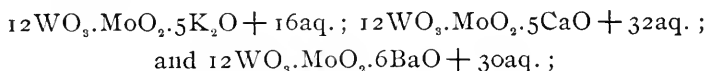
Molybdicotungstates.

When acid molybdate of ammonium is boiled with chlorhydric acid and potassic iodide, and the deep orange-colored liquid is precipitated with ammonia, a brown precipitate of $\text{Mo}(\text{OH})_4$ is thrown down, which, after thorough washing, is readily soluble in a solution of 12 : 5 sodic tungstate, forming a deep orange-red liquid. Potassic bromide gives a buff-colored crystalline precipitate, which is soluble in boiling water, and crystallizes on cooling in small pale-brown scales. Ammonic chloride gives a similar salt, as do also the chlorides of barium, strontium, and calcium. All these salts are soluble in hot water, and separate from the solution in pale brown crystals. In preparing the potassium salt a large excess of potassic bromide should be used ; the bromide in this, as in many other cases, appears to be preferable to the chloride and nitrate. In these salts the molybdic dioxide may be easily and accurately determined by titration with permanganate, after adding sulphuric acid. The solutions of the molybdicotungstates readily absorb oxygen from the air, forming molybdic tetroxide, a fact which must be taken into account in analysis.

Molybdic hydrate, $\text{Mo}(\text{OH})_4$, quickly reduces MoO_3 in a solution of 14 : 6 ammonium salt, and gives a fine blue liquid, which probably contains Mo_2O_6 or $\text{MoO}_2 + \text{MoO}_3$. When a very cold solution of ammonic molybdate is employed, and molybdic hydrate is added in small portions at a time, the solution becomes yellow, then quickly green, and finally blue. It is possible that a molybdicomolybdate, $m\text{MoO}_2 \cdot n\text{MoO}_3 \cdot p\text{R}_2\text{O}$, is formed at first. Molybdic hydrate reduces both molybdic and tungstic tetroxides in phosphomolybdates and phospho-

¹ A REBUS GERENDIS SENECTUS ABSTRAHIT.—Cicero, *Cato Major*.

tungstates. Analyses of the potassium, calcium, and barium molybdictungstates were made with salts which perhaps were not absolutely pure. The formulas obtained appeared to be respectively



but these are given with much reserve. In these the molybdenum was determined by titration with permanganate, and the sum of the molybdic and tungstic teroxides, after oxidation, by precipitation of the neutral solution with calcic or baric chloride. Tungstic teroxide could then be determined by difference.

It seems at least probable that tungsticomolybdates corresponding to molybdictungstates, as, for example,



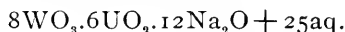
also exist.

Uranoso-Tungstates.

When uranic oxide is dissolved in dilute sulphuric acid, and the solution is treated with metallic zinc, a solution of sulphate of uranic dioxide is formed which, after a time, deposits a gray-green powder insoluble in cold water, and, probably, a basic sulphate. This body treated with a solution of 12 : 5 sodic tungstate gives at once an olive-green crystalline salt very insoluble in hot water. The supernatant liquid has a peculiar reddish tint. The dark olive-green salt is oxidized by boiling with nitric acid and gives a yellowish-white mixture, or possibly compound, of uranic and tungstic teroxides, easily decomposed by boiling with caustic alkalies, with separation of uranic oxide and formation of sodic tungstate. A solution of 12 : 5 potassic tungstate acts in the same manner upon the uranious salt, giving also an olive-green crystalline salt and a brown-red solution. Similar results were obtained with acid ammonic tungstate. After drying for some days upon paper, the sodium salt was analyzed by Dr. Loeb:

0.4436 gram lost with WO_4NO_2 0.0331 gram = 7.46 per cent.
 { 0.9861 gram gave 0.3954 gram WO_3 = 40.09 per cent.
 { 0.9861 gram gave 0.3360 gram UO_3 and KMnO_4 = 34.08
 { per cent.

The analyses lead to this formula :



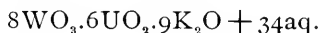
		Calculated.	Found.
8 WO_3	1856	39.69	40.09
6 UO_3	1626	34.77	34.08
12 Na_2O	744	15.92	16.46 (diff.)
25 H_2O	450	9.62	9.47
	<hr/>	<hr/>	
	4676	100.00	

The water determination was made by heating with sodic tungstate and determining the loss of weight. In the fusion the UO_2 is completely reoxidized to UO_3 . Hence a correction must be applied to the water, which in the above case amounts to 2.01 per cent to be added. As the salt could not be recrystallized, it was doubtless not perfectly pure.

The olive-green potassium salt is also insoluble in hot water and in chlorhydric acid. It reduces silver and mercury from their nitrates, and appears to undergo double decomposition with baric and calcic chlorides. This salt was also analyzed by Dr. Loeb :

{ 1.3260 grams gave 0.4997 gram WO_3 = 37.69 per cent.
 { 1.3260 grams gave with KMnO_4 gram UO_3 = 33.21 per cent.
 0.9275 gram lost on ignition with WO_4Na_2 0.0833 gram =
 8.98 per cent.

The analyses lead to the formula :



		Calculated.	Found.
8 WO_3	1856	37.58	37.69
6 UO_3	1626	32.92	33.21
9 K_2O	846	17.12	16.60 (diff.)
34 H_2O	612	12.38	12.50
	<hr/>	<hr/>	
	4940	100.00	

The potassic salt corresponds in constitution to the sodic salt if we write it :



Silico-Molybdates.

The existence of definite silico-molybdates appears to have been first observed by Parmentier,¹ who obtained potassium, sodium, and ammonium salts by the action of alkaline silicates upon alkaline molybdates in presence of nitric acid. The free acid has the formula $12\text{MoO}_3 \cdot \text{SiO}_2 + 26 \text{ aq.}$ I have devised another method of preparing this class of salts, which may perhaps be generalized in its application. When a solution of fluosilicic acid is poured into one of 14 : 6 molybdate of ammonium, no precipitate is formed, but the solution becomes yellow. On evaporation, a bright yellow crystalline body separates in large quantity. When normal sodic molybdate, MoO_4Na_2 , is strongly acidulated with chlorhydric acid, the addition of fluosilicic acid gives at once a bright yellow color. The solution obtained in this manner gives no precipitate in the cold with ammonic chloride, but on boiling and shaking for a few minutes a beautiful bright yellow crystalline precipitate is thrown down in abundance. This is slightly soluble in hot water to a yellow liquid. A solution of fluosilicic acid mixed with one of an acid potassic molybdate forms no precipitate, but the mixture is yellow, and on evaporation to dryness upon a water-bath yields a highly crystalline yellow powder. Much molybdic teroxide is at the same time reduced to blue oxide. The yellow solutions of the silicomolybdates of potassium and sodium give with nitrate of croceo-cobalt a beautiful orange crystalline precipitate, which is insoluble in cold water and readily washed and dried. The bright yellow silicomolybdate of ammonia, after careful washing, was analyzed:

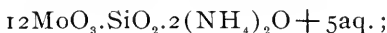
0.7963 gram lost on ignition with WO_4Na_2 0.0750 gram $\text{NH}_3 + \text{H}_2\text{O} = 9.42$ per cent.

0.5279 gram left on ignition 0.0158 gram $\text{SiO}_2 = 2.99$ per cent.

0.6504 gram gave 0.0339 gram $(\text{NH}_4)_2\text{O} = 5.22$ per cent.

0.5817 gram gave 0.03045 gram $(\text{NH}_4)_2\text{O} = 5.23$ per cent.

The analyses correspond to the formula



which requires:

¹ Compt. rend., 92, 1234; 94, 213.

		Calculated.	Found.
12 MoO ₃	1728	87.18	87.58 (diff.)
SiO ₂	60	3.03	3.00
2 (NH ₄) ₂ O	104	5.24	5.22 5.23
5 H ₂ O	90	4.55	4.20
	<hr/>	<hr/>	
	1982	100.00	

The silica was determined by igniting the salt with free access of air until all the molybdic oxide was expelled. The reactions of a solution of sodium salt were as follows: No precipitate with baric and calcic chlorides; none at first with potassic bromide, but, on standing, bright yellow crystals formed; a sulphur-yellow crystalline precipitate with mercuric nitrate and a beautiful bright orange-yellow highly crystalline precipitate with mercurous nitrate; a very pale yellow crystalline precipitate with argentic nitrate, and a pale yellow fine-grained crystalline precipitate with thalious nitrate. Pechard¹ has obtained the same salt by precisely the same process as that which I have employed, and has priority in publication. I have also obtained a titanio-molybdate and a zirconio-molybdate by similar methods, but have not analyzed them. Pechard has described beautiful salts of the two series, and rendered further work on my part unnecessary.

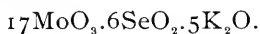
Selenoso-Molybdates.

When 24:1 phosphomolybdate of potassium is boiled with a solution of potassic selenite, SO₃K₂, it readily dissolves to a perfectly clear and colorless liquid, which after an hour deposits beautiful large granular colorless crystals in abundance. These are readily soluble in hot water, and crystallize from the solution without change, except that large transparent colorless crusts are obtained. Of this salt, analyzed by Mr. G. W. Patterson:

- { 1.1360 grams gave 0.1503 gram Se = 13.23 per cent. = 18.09 per cent. SeO₂.
- { 1.1360 grams gave 0.7772 gram PtCl₆K₂ = 13.27 per cent. K₂O.
- 0.9570 gram lost up to 175° C. 0.0058 gram H₂O = 0.61 per cent.

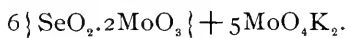
¹ Compt. rend., 117, 691-694; Cited Ztschr. anorg. Chem., 6, 200.

Deducting the small percentage of water, the analyses correspond to the formula



		Calculated.	Found.
17MoO ₃	2448	68.81	68.45
6SeO ₂	648	18.16	18.20
5K ₂ O	472	13.23	13.35
	<hr/>	<hr/>	
	3568	100.00	

The formula may also be written,



The selenium was determined by reduction with sulphurous acid and the molybdic oxide by difference. In spite of the mode of preparation, the salt did not contain phosphoric pentoxide. On repeating the preparation of the salt I obtained different results, the proportions used being probably not the same. The solution deposited at first groups of colorless crystals, and then gave, after further evaporation, a white granular crystalline salt. The grouped crystals seemed at first to be quite insoluble in water, but, when boiled, dissolved, and then crystallized out very readily. Perhaps more than one salt was formed in this operation. The solution of the salt analyzed gave pale yellow crystalline precipitate with argentic and mercurous nitrates.

Selenoso-Tungstates.

When ammoniac tungstate is boiled with a solution of SeO_3H_2 , it readily dissolves to a pale yellow solution, which almost immediately gives beautiful shimmering scales in a pale yellow mother-liquor. These pass at once through a filter and are difficult to separate and wash. Potassic tungstate also readily dissolves in a solution of selenious acid, forming a pale yellow solution which on heating suddenly becomes opaque, while a pale yellow precipitate is thrown down. When washed by decantation with cold water, both the ammoniac and potassic salts have a distinct pale yellow color. When a solution of selenious acid is mixed with one of 12:5 sodic tungstate and a solution of potassic bromide is added, a white precipitate in very minute granular crystals is formed, settling

rather slowly, and very slightly soluble in hot water. A solution of argentic nitrate gave, with the well-washed salt, large very pale yellow crystalline flakes. Mercurous nitrate gave a pale yellow crystalline precipitate. A solution of selenious acid mixed with one of 24:1:2 sodic phosphotungstate gave a white granular precipitate very slightly soluble in hot water. After careful washing, this gave, on boiling with argentic nitrate, a perfectly white crystalline salt; a bright yellow crystalline precipitate with mercurous nitrate; and a white crystalline precipitate with baric chloride. It is possible that phospho-selenoso-tungstates are formed in this manner.

Pechard¹ has recently described salts of two series of molybdo-selenites, as he terms them, having respectively formulas which would indicate that they are derivatives of the acids $4\text{H}_2\text{O}.3\text{SeO}_2.10\text{MoO}_3$, and $2\text{H}_2\text{O}.\text{SeO}_2.5\text{MoO}_3$.

The same chemist has also described a very interesting series of salts, which he terms molybdo-sulphites, embraced under the general formula



Telluroso-Molybdates and Tungstates.

Klein² many years since also observed the existence of complex acids containing tellurous and telluric oxides and tungstic oxide. So far as I am aware, no analyses have been published. A preliminary notice of my own work was communicated to the Harvard Chemical Club, February 12, 1884.³

When a solution of TeBr_6K_2 is boiled with a large excess of water, the salt is completely decomposed into bromhydric and tellurous acid, TeO_3H_2 . A solution of 14:6 acid molybdate of ammonium readily dissolves this last on boiling, and the clear filtered solution soon deposits beautiful granular colorless crystals in quantity. It is best to use an excess of tellurous acid. The telluroso-molybdate is much less soluble than the acid molybdate of ammonia, and may be redissolved and recrystallized without apparent decomposition. When a solution of the TeBr_6K_2 is mixed with one of the acid molyb-

¹ Compt. rend., **116**, 1441-1444; **117**, 104-106.

² Bull. Soc. Chim. (Paris), [2], **42**, 169.

³ See also Ber. d. chem. Ges., **18**, 1089, August, 1884.

date, a very pale yellow precipitate is formed. After standing, small bright yellow crystals also appear. The white precipitate is probably only tellurous acid. When freshly precipitated tellurous acid is boiled with a strong solution of an acid potassic tungstate, it does not dissolve, but changes character and becomes more distinctly crystalline. A solution of TeBr_6K_2 gives with one of $24:1:2$ phosphotungstate of sodium a very white granular precipitate, which is insoluble, and may be washed with boiling, but then settles slowly. The tellurium employed was the best commercial product, and doubtless not absolutely pure. If, as has been supposed, two different metals are embraced under the name, it is possible that the compounds of the two oxides with molybdic and tungstic oxides may afford means of separation in consequence of differences in composition and properties. Should tellurium be hereafter found to possess a technical value or interest, an abundant supply can be furnished by the mines of Colorado. The very high cost of the metal at present has prevented further study on my part.

Cerico-Molybdates.

When ceric fluoride, CeF_4 , is boiled in a platinum dish with $14:6$ molybdate of ammonium, the solution quickly becomes yellow, and soon deposits a fine yellow crystalline salt, which may be washed with cold water, in which it is but slightly soluble. It contains molybdic teroxide, ceric oxide, and ammonia. Basic ceric nitrate treated with a solution of hydro-potassic fluoride, KF_2H , changes character at once and becomes flocky-crystalline. After washing with cold water, boiling with $14:6$ molybdate of ammonium dissolves but little, but the salt becomes bright sulphur yellow and crystalline and is practically insoluble in water. The best method of preparing this salt consists in first preparing pure basic nitrate of cerium¹ free from lanthanum and didymium (neodymium and praseodymium). This is to be dissolved in nitric acid and the solution diluted. Acid potassic fluoride then precipitates a nearly white flocky salt, which dissolves readily in a boiling solution of $14:6$ molybdate of ammonium

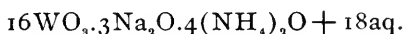
¹ See my paper in *Am. J. Sci.*, **37**, 352.

to a yellow solution, and crystallizes from this. It will probably be better to boil with a solution of an acid sodic molybdate, as this yields a soluble sodic salt, the solution of which gives with ammoniac chloride a yellow crystalline precipitate of an ammonium salt, which will make a good starting-point for further investigations.

When the ceric fluorine salt, prepared as above with KF_2H , is boiled with 10 : 4 sodic tungstate, a fine bright yellow solution is formed which gives a beautiful orange, crystalline precipitate with nitrate of croceo-cobalt. In preparing the fluorine compound it is best to add a cold filtered solution of KF_2H to the basic ceric nitrate diffused in cold water, and not to heat at all. Ceric hydrate dissolves with difficulty in solutions of acid tungstates and molybdates, more easily when precipitated from cold solutions.

NOTE ON CERTAIN TUNGSTATES, AND ON A NEW PHOSPHOTUNGSTATE.

In other instalments of my work I have endeavored to show¹ that there exists a special class of metatungstates, of which the lowest term has the general formula $4\text{WO}_3.\text{RO}$, and the highest the general formula $24\text{WO}_3.11\text{R}_2\text{O}$. This view appeared to be supported both by my own work and by that of Marignac, but has not found favor with chemists, and has in fact, so far as I am aware, passed wholly unnoticed. The highest term actually obtained by me² appeared to have the formula



The only complete analysis made agreed well with this formula, and differed very materially from that of the 12 : 5 ammonia-sodic tungstate. As it has been asserted, however, that the two are identical, Mr. Charles D. Smith has made in my laboratory four analyses with portions of the salt which had been preserved. The analyses are as follows:

0.7226 gram gave 0.6038 gram $\text{WO}_3 = 83.55$ per cent.

1.1598 grams gave 0.9687 gram $\text{WO}_3 = 83.54$ per cent.

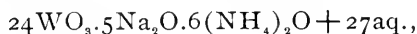
1.3281 grams gave 1.1091 grams $\text{WO}_3 = 83.51$ per cent.

¹ *Proc. Am. Acad.*, 15, 15.

² *Ibid.*, 16, 76.

- 1.4740 grams gave 1.2309 grams $\text{WO}_3 = 83.50$ per cent.
 1.2726 grams gave 0.0604 gram $(\text{NH}_4)_2\text{O} = 4.75$ per cent.
 1.0901 grams gave 0.0508 gram $(\text{NH}_4)_2\text{O} = 4.66$ per cent.
 1.1360 grams gave 0.0532 gram $(\text{NH}_4)_2\text{O} = 4.67$ per cent.
 0.6756 gram gave 0.0318 gram $(\text{NH}_4)_2\text{O} = 4.72$ per cent.
 4.4687 grams lost on ignition 0.5292 gram NH_3 and $\text{H}_2\text{O} = 11.84$ per cent.
 3.0697 grams lost on ignition 0.3638 gram NH_3 and $\text{H}_2\text{O} = 11.84$ per cent.
 4.6030 grams lost on ignition 0.5444 gram NH_3 and $\text{H}_2\text{O} = 11.82$ per cent.
 3.3885 grams lost on ignition 0.4014 gram NH_3 and $\text{H}_2\text{O} = 11.84$ per cent.

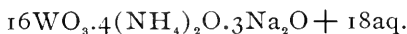
The analyses correspond to the formula



which requires:

		Calculated.	Mean.	I.	II.	III.	IV.
24 WO_3	5568	83.40	83.52	83.55	83.54	83.51	83.50
6 $(\text{NH}_4)_2\text{O}$	310	4.68	4.70	4.75	4.66	4.67	4.72
5 Na_2O	312	4.65	4.65
27 H_2O	486	7.27	7.13	7.08	7.14	7.16	7.11
	<hr/>	<hr/>					
	6676	100.00					

The sodic oxide is determined by difference. The analyses agree rather more closely with the new formula than with that formerly given, which I will cite for the sake of comparison:



This requires

		Calculated.	Found.
16 WO_3	3712	83.77	83.94
4 $(\text{NH}_4)_2\text{O}$	208	4.69	4.64
3 Na_2O	186	4.20	4.21
18 H_2O	324	7.32	7.21
	<hr/>	<hr/>	
	4430	100.00	

It is certainly difficult to decide between these two formulas, only it must be observed that the higher formula is derived from the mean of four analyses, which agree well with each other, and has therefore the weight of analytical evidence in

its favor until further research shall prove its inaccuracy. Still another formula has been proposed by Von Knorre,¹ who writes $12\text{WO}_3 \cdot 3(\text{NH}_4)_2 \cdot 2\text{Na}_2\text{O} + 13\text{aq.}$, which requires 84.41 per cent. WO_3 , 4.73 per cent. $(\text{NH}_4)_2\text{O}$, 3.76 per cent. Na_2O , and 7.10 per cent. H_2O . The correspondence between the results of the analyses and the data required by the formula is much less than with the formula which I first gave and which Von Knorre rejects, and of course still less than with the new formula.

New Phosphotungstate.

Pure normal sodic tungstate was mixed in solution with sodic ortho-phosphate, $\text{PO}_4\text{Na}_2\text{H} + 12\text{aq.}$, in the proportion of twelve molecules of the first to one of the second salt, and chlorhydric acid added in small excess. A phosphotungstate crystallized from the solution, and was redissolved and twice recrystallized. The new salt was in fine colorless crystals, less soluble than the now well-known salt which has the formula $24\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2\text{Na}_2\text{O} + 27\text{aq.}$ The salt was dried on paper for analysis. It effloresced or became opaque in dry air. Mr. Charles D. Howard obtained the following results on analysis.

1.4941 grams lost on ignition with WO_4Na_2 0.1078 gram H_2O
 $= 7.21$ per cent.

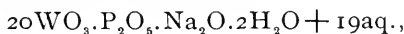
1.4502 grams lost on ignition with WO_4Na_2 0.1046 gram H_2O
 $= 7.21$ per cent.

1.0950 grams gave 1.0019 grams $\text{WO}_3 + \text{P}_2\text{O}_5 = 91.49$ per cent.

1.1950 grams gave 1.0975 grams $\text{WO}_3 + \text{P}_2\text{O}_5 = 91.58$ per cent.

1.6782 grams gave 0.0720 gram $\text{WO}_3 + \text{P}_2\text{O}_5 = 2.74$ per cent.
 P_2O_5 .

The analyses lead to the formula

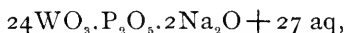


which requires :

		Calculated.	I.	II.
20WO_3	4640	88.85	88.75	88.84
P_2O_5	142	2.73		2.74
Na_2O	62	1.18		1.25
$21\text{H}_2\text{O}$	378	7.24	7.21	7.21
	<hr/> 5222	<hr/> 100.00		

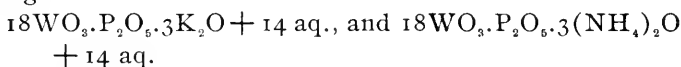
¹ Ber. d chem. Ges., 19, 823.

The only 20 : 1 phosphotungstate which I have hitherto described¹ contained 6 molecules of base (BaO), and perhaps the new salt should be written $20\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{Na}_2\text{O} \cdot 5\text{H}_2\text{O} + 16 \text{ aq.}$ With respect to its formation with the proportions given, I may remark that I have in repeated trials failed to obtain the salt



by mixing sodic tungstate and phosphate in the exact theoretical proportions and adding chlorhydric acid to the mixed solutions. The quantity of phosphate necessary to be added is much more than 1 molecule for 12 molecules of the tungstate. This remark appears to have been made by other chemists also.

Kehrmann² has recently described phosphotungstates which come under the general formula $18\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3\text{RO}$, the salts being

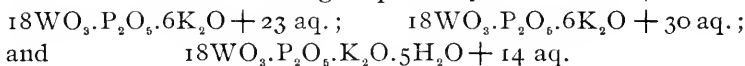


He gives to the acid the name "Phospholuteo-wolframsäure"; but though there is little doubt that there is here a hitherto undescribed series, the analyses are not satisfactory.

In another part of this paper I have described three salts of a phosphotungstic acid which would have the formula



the salts themselves having respectively the formulas,



These salts are, however, colorless, and if we admit the accuracy of Kehrmann's formulas, there must be two isomeric series. Kehrmann appears to have been wholly unacquainted with my work.

Experiments to determine the relations of WS_4K_2 , MoS_4K_2 , and $\text{WS}_2\text{O}_2\text{K}_2$, to phosphates and arsenates have not led to definite results, though there seemed to be a relation of some kind. The same statement applies to the various oxyfluorides of molybdenum and tungsten.

In a communication made to the British Association³ at the

¹ Proc. Am. Acad., 16, 127. This Journal, 2, 282.

² Ztschr. anorg. Chem., 4, 138, 386.

³ Report for 1884, p. 670.

Montreal meeting, in 1884, I stated that complex acids existed into which platinum chloride entered, as, for instance, compounds of the type $2\text{PtCl}_2 \cdot \text{R}_2\text{O}_3$. Since then I have made various communications on the same subject to the Harvard Chemical Club. I regard these compounds as respectively phosphoric, arsenic, and antimonie oxides, in which 2PtCl_2 replaces O_2 . A great amount of work on the subject has been done, but as it is at least possible that a very different view of the subject may be taken, I will reserve the results of my work for another occasion.

NEWPORT, R. I., August, 1894.

[To be continued.]

Contribution from the Chemical Laboratory of Dartmouth College.

CUPRIC HYDRIDE.

BY EDWIN J. BARTLETT AND WALTER H. MERRILL.

In the course of experiments recently undertaken to confirm the equation for the reaction between copper sulphate and hypophosphorous acid, it was found that the quantity of hydrogen set free depends, not upon the amount of cuprous hydride formed, but upon the quantity of hypophosphorous acid present. Further investigation showed that this evolution of gas was caused by the copper sponge which results from the decomposition of cuprous hydride, and that the action continues as long as there is hypophosphorous acid present. R. Engel, in a recent article,¹ says that palladium hydride will oxidize barium hypophosphite to the phosphite with the evolution of hydrogen; and that the action is a continuous one with apparently no effect upon the hydride. This copper sponge has always been called pure copper; if so, other forms of the metal ought to react in the same manner. Copper wire, foil, and the powder formed by precipitation with hypophosphorous acid in an excess of copper sulphate solution were found to have no action upon the acid, but finely powdered cupric oxide, when reduced by hydrogen, readily oxidizes the acid. This fact would point to the conclusion that either a new hydride of copper is formed by the decomposition of cuprous hydride in the presence of hypophosphorous acid, or that this precipitate contains occluded hydrogen.

¹ Compt. rend., 110, 786.

The quantity of hydrogen in this substance was determined in the following manner: The copper sponge was first transferred to boiling water, care being taken not to remove with it any of the metallic copper which is formed upon the sides of the vessel. After thorough washing, it was boiled for half an hour to remove any traces of free hydrogen, or of the acid which might still be retained, and was then transferred to a weighed crucible. The excess of water was absorbed by filter paper and the hydride dried in an air-bath at about 60°. After weighing, it was oxidized at a dull red heat until the resulting weight was constant. The remaining copper was then determined as the oxide.

I. 0.0079 gram of the substance gave 0.0096 gram of cupric oxide.

II. 0.0088 gram of the substance gave 0.0107 gram of cupric oxide.

III. 0.0198 gram of the substance gave 0.0239 gram of cupric oxide.

IV. 0.0228 gram of the substance gave 0.0276 gram of cupric oxide.

	Calculated for CuH_2 .	I.	Found. II.	III.	IV.
Copper	96.93	97.09	97.15	96.44	96.72
Hydrogen by difference..	3.07	2.91	2.85	3.56	3.28

Each of these four analyses was made with a sample independently prepared, and the agreement in the results plainly indicates that a definite compound is formed.

If this copper sponge is a fixed compound we should expect to find, as we do, that cupric oxide reduced by hydrogen has the same composition, since it acts in the same way with hypophosphorous acid. In experiments V and VI, cupric oxide was reduced in a current of hydrogen until the resulting weight was constant, then washed, and the percentage of copper determined as before:

V and VI. 0.1169 and 0.0915 gram of the substance gave, respectively, 0.1421 and 0.1111 gram of cupric oxide.

In experiments VII and VIII, the cupric oxide was reduced by hypophosphorous acid in excess until the hydride had been formed, and it, in turn, had oxidized the remaining hypophos-

phorous acid. The reaction was considered complete when hydrogen ceased to be liberated.

VII. 0.1953 gram of the substance gave 0.2362 gram of cupric oxide.

VIII. 0.0964 gram of the substance gave 0.1171 gram of cupric oxide.

	Calculated for CuH ₂ .	V.	Found. VI.	VII.	VIII.
Copper	96.93	97.12	97.02	96.63	97.05
Hydrogen by difference..	3.07	2.88	2.98	3.37	2.95

The above process was tested by blank experiments in which the copper powder, formed by the decomposition of cuprous hydride in a solution having an excess of copper sulphate, was used. Four determinations were made, and in each case the copper found in the cupric oxide was between 99.60 per cent. and 99.97 per cent. of the copper in the substance taken.

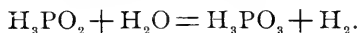
Properties of Cupric Hydride.

Cupric hydride, when freshly prepared, is a reddish-brown sponge-like mass, which, however, changes to a chocolate-colored powder on being freed from acid and boiled for some time. On drying, it retains this color but, if heated with a very dilute solution of hypophosphorous acid, the particles collect again into flakes and the reddish color returns. It is only when it has this appearance that hypophosphorous acid is oxidized. When heated in the air above 100°, it is unchanged, or but partially decomposed, until a heat is reached sufficient to oxidize the copper. Like the cuprous hydride, it dissolves in warm concentrated hydrochloric acid with evolution of hydrogen, but less readily, and with the formation of the cupric instead of the cuprous salt. As mentioned before, it will oxidize hypophosphorous acid to phosphorous acid, liberating hydrogen. This action was found to be a continuous one and has no effect upon the hydride, and will even take place at the temperature of the room. Böttger,¹ Graham² and others have shown that hydrogen, when in combination with a metal, acts as a reducing agent, especially in the cases of palladium and platinum hydrides. So in this case when

¹ Ber. d. chem. Ges., 6, 1396.

Proc. Roy. Soc., 17, 212.

cupric hydride is introduced into a solution where the water molecule is weakened by the attraction between hypophosphorous acid and its own oxygen, the hydride is a reducing agent of sufficient strength to destroy the remaining bond and separate the molecule. The volume of hydrogen liberated corresponds to the following equation :



When hypophosphorous acid is concentrated to a thick syrup it is decomposed by cupric hydride, giving off non-inflammable phosphoretted hydrogen and hydrogen gases. In this case the action is like that of nascent hydrogen, and, as before, the hydride appears to lose none of its hydrogen. The acid, on the other hand, when decomposed by heat liberates spontaneously inflammable phosphuretted hydrogen, and the heat required is much greater than that used with the hydride.

Gladstone and Tribe,¹ while investigating the analogy between the action of their copper-zinc couple and hydrogen occluded by metals, found the hydrogen in combination with copper reduces a solution of potassium chlorate to the chloride, and also potassium nitrate to the nitrite and ammonia. Graham² says that palladium hydride will readily reduce a solution of potassium ferricyanide to the ferrocyanide. Cupric hydride formed by the action of hypophosphorous acid on a solution of copper sulphate, easily produces these reductions. With arsenious acid, however—which is also reduced by palladium hydride—there is found to be little or no action. A slight darkening in the color of the solution appeared on boiling, but did not seem to increase when more arsenious acid was added. Yet when a few drops of hypophosphorous acid were added the liquid became darker and arseniuretted hydrogen was liberated.

It has been shown³ that the activity of the copper-zinc couple is greatly increased by ignition in a current of hydrogen gas. This increase is due probably to the formation of cupric hydride. The union of copper, zinc, and hydrogen

¹ J. Chem. Soc., **33**, 308, 1878.

² Proc. Roy. Soc., **17**, 212.

³ J. Chem. Soc., **35**, 567, 1879.

was found by Gladstone and Tribe¹ to be more powerful for effecting the decomposition of certain organic substances than the electric current derived from a battery of 100 Grove's cells. Cupric hydride alone is a moderate reducing agent but, in conjunction with zinc in the copper-zinc couple, or with other oxygen-seeking substances, as hypophosphorous acid, becomes an extremely powerful reducing agent.

It has been found that hypophosphorous acid reacts with almost all the metallic oxides, either forming hypophosphites or reducing them to a metal-like precipitate, which, in several cases, already, we have found to be a definite hydride.

Contribution from the Laboratory of the University of California.

ACTION OF LIGHT ON LEAD BROMIDE.

BY R. S. NORRIS.

In an article² on Double Halides, H. L. Wells mentions the fact that lead bromide is darkened by light. I had noticed the action a short time before the appearance of this article and had made a few experiments to confirm it. The discovery immediately suggested an analogy to the similar change of color in the silver halides, so an attempt was made to ascertain the nature of the action.

The darkening is much slower than in the case of the silver salts, and takes place only on the merest surface of the exposed substance ; it was therefore found difficult to obtain a product all of which was darkened. This was overcome as much as possible by exposing it in a thin layer between two pieces of plate glass. The layer was formed by spreading the finely powdered bromide, as evenly as possible, over one of the plates, and then rubbing the plates together until the layer was even and transparent enough to read print through it. The plates were clamped together and exposed to the light for several days. The product was black, and on being dissolved in water, with the addition of a drop or two of nitric

¹ *Ibid.*, **31**, 561, 1877.

² *Am. J. Sci.*, **45**, 134.

acid,¹ left a small amount of metallic lead, equal to about 1 per cent. of the original substance. Analysis showed the loss of 2.4 per cent. of the bromine. It seems very probable from this that the action is one of simple dissociation between the lead and bromine.

Another experiment similar to the above, using large glass plates (2×3 feet) with a space of about a millimeter between them, and exposed to bright sunlight for two weeks, gave a product lighter in color than that exposed for a shorter time, and entirely soluble in water acidulated with nitric acid. In this experiment the metallic lead which was first formed by dissociation was probably oxidized on further exposure.²

In order to ascertain whether pure lead bromide is decomposed by light, a small amount of the pure salt was prepared in the following manner; Lead nitrate (De Haen, puriss.) was recrystallized, and the most perfect crystals selected, washed, and dissolved in water. The solution was made strongly acid with nitric acid, and lead peroxide precipitated from it electrolytically, in a platinum dish, according to the method of Smith. The peroxide was washed by decantation, dried, and carefully heated until it was all converted into oxide, PbO. This was treated with a solution of hydrobromic acid, prepared by the direct union of hydrogen and bromine. The apparatus used in preparing the acid was entirely of glass except the roll of platinum foil over which the gases passed; and the hydrogen and bromine were both carefully purified. The lead oxide dissolved completely. The excess of acid was evaporated off, and the precipitate recrystallized from a water solution several times. The crystals which were finally obtained were assumed to be pure lead bromide. They darkened rapidly in the light.

A number of experiments were made to determine the action under different conditions. Exposed under water the action is very slow, taking several days exposure before any darkening is noticed. The fused bromide is darkened rap-

¹ In dissolving the darkened substance it was found necessary to use a little nitric acid, because dry lead bromide does not entirely dissolve in water,—presumably on account of the formation of an oxybromide.

² Cf. W. Schmidt: "The Decomposition of Lead Chloride by Light;" *Ann. der Phys. Pogg.*, **127**, 493.

idly. Two tubes containing a small amount of lead bromide, were filled with dry oxygen and hydrogen, respectively, sealed, and exposed to the light; decomposition took place with equal rapidity in both cases, and no difference could be noticed in the action.

The evidence so far seems to be in favor of simple dissociation as the explanation of the reaction, but not enough has been obtained to furnish proof of it. I hope to be able, by further experiments, to determine whether or not this hypothesis is the correct one.

Contributions from the Chemical Laboratory of Purdue University.

XII.—THE ACTION OF AMMONIA UPON DEXTROSE.

BY W. E. STONE.

The behavior of glucose toward ammonia has been studied by several investigators, but always with results that have discouraged further attention. By heating glucose with ammonia, Thenard¹ obtained a brown, amorphous body which had a bitter taste, contained varying amounts of nitrogen, and yielded up ammonia upon heating with alkalis. A similar substance was observed by Schoonbrodt² on treating sugar with ammonia in the presence of phosphorus pentoxide. Tanret³ describes two liquid, basic compounds obtained by treating dextrose with strong ammonia; *viz.*, α -glycosine, $C_6H_8N_2$, boiling at 136° , and β -glycosine, $C_7H_{10}N_2$, boiling at 160° . Here it is evident that the dextrose molecule has undergone deep-seated changes. Finally, Laborde⁴ noted a crystalline substance resulting when ammonia was passed over dextrose; this body did not receive further attention.

The aldehyde character of dextrose, which has been established beyond doubt, would lead us to expect a compound between it and ammonia of the class of the well-known aldehyde-ammonias. But this, as well as several other characteristic aldehyde-reactions, fails in the case of dextrose and other

¹ Compt. rend., **52**, 444.

² *Ibid.*, **52**, 1071.

³ Ber. d. chem. Ges., **18**, 500.

⁴ Jsb. Chem., 1874, 83.

aldose sugars, notably the fuchsin-sulphurous-acid reaction and the reaction with acid potassium sulphite. The ammonia-reaction may now, however, be included in those to which dextrose and, undoubtedly, the other aldoses respond.

I have prepared a crystalline compound of dextrose and ammonia which is fairly stable under ordinary conditions and exhibits the composition and reactions of an ammonia-aldehyde compound of the formula $C_6H_{12}O_6 \cdot NH_3$.¹

If dextrose be suspended in absolute alcohol, which has been saturated with ammonia gas, it becomes dissolved to an appreciable extent, or, if dry ammonia gas be passed into absolute alcohol in which anhydrous dextrose is suspended, solution occurs and a slight rise in temperature may be noted. Solution takes place slowly, but after standing for a week or more in a closed vessel the solution, upon exposure to the air, shows a marked sensitiveness to carbonic dioxide, the whole solution becoming turbid. If the breath or a current of carbonic dioxide be passed through the solution, immediate precipitation occurs. The precipitate is amorphous and viscous, with a sharp biting taste. After drying over sulphuric acid the substance becomes hard and brittle. It is readily soluble in water, reduces Fehling's solution strongly, gives off ammonia when warmed with alkalis and carbonic dioxide on treatment with acids. If hydrochloric acid be added to the original alcoholic solution, a flocculent precipitate is formed. Both of these substances are probably mixtures of dextrose and ammonium salts, but their precipitation, in the manner described, indicates that the dextrose is in solution, that its solubility is dependent upon the ammonia present, and that, probably, the two are in combination. By a different procedure, a definite compound of this kind has been obtained.

The alcoholic solution which has been saturated with ammo-

¹ The studies upon which this paper is based were begun by me early in the year 1894, and only after their completion as here presented did I learn of the work of C. A. Lobry de Bruyn and A. P. Franchinmont (*Receuil trav. chim.*, **12**, 286-89). These authors mention the preparation of crystalline compounds of ammonia with dextrose, galactose, and levulose from alcoholic solution. The details of their work are not at hand, but inasmuch as my work presents some points not touched upon by them and has been carried on independently, I desire to publish the results and to continue the investigation, especially since upwards of two years have passed since the publication of Messrs. de Bruyn and Franchinmont without any new announcements from them.

nia and stood over dextrose, with frequent agitation for upwards of ten days, is decanted into a separate vessel and kept closed from the air. In from ten to fourteen days more, there begins a deposition of warty crystal growths upon the walls of the flask. These increase gradually until they finally converge, and flocculent crystalline masses are formed throughout the liquid. The entire process, from beginning to end, occupies about a month. On filtering off the product, the alcoholic liquid is found to be no longer sensitive to the carbonic dioxide of the air, but when allowed slowly to evaporate in a desiccator, it deposits a considerable quantity of an amorphous substance which has not been further studied. It is evident, however, from this that not all of the dissolved dextrose is transformed into the crystalline product. The yield of crystals is not large; 250 cc. of alcohol saturated with ammonia, as described, and acting upon 15 grams of dextrose, yielded about 5 grams of the crystalline material. The undissolved dextrose was gradually changed into a brown, viscous mass which has not been further investigated.

The crystalline product referred to is snow-white, and apparently stable under ordinary conditions. It is sweet to the taste, readily soluble in water, reduces Fehling's solution readily, and might be mistaken for a specimen of pure anhydrous dextrose. It is insoluble in cold alcohol and ether, but may be dissolved in 80-per cent. alcohol upon warming. An aqueous solution of the compound shows an alkaline reaction with litmus paper. Ammonia is given off on warming with caustic soda, or when the material is strongly heated by itself.

The material melted sharply between 122° and 123° (uncorr.). The percentage of ammonia was determined by distilling with caustic soda into standardized acid. In this way 8.74 per cent. of ammonia was obtained from a freshly prepared sample. For the compound $C_6H_{12}O_6 \cdot NH_3$, the theoretical percentage of ammonia is 8.63, and for a compound of the hydramid class, $(C_6H_{12}O_6)_3N_2$, 6.53 per cent. This leaves little doubt as to the nature of the compound, and this conclusion is further supported by its general behavior.

The specific rotation in watery solution was found to be $(\alpha)_D = 22^{\circ}$ to 22.7° . No birotation was observed. In this

connection it is of interest to recall the observation of Tollens, that small quantities of ammonia added to solutions of sugars which normally exhibit bi- or multirotation, destroyed this property at once.

Apparently, this compound is stable at ordinary temperature, although analysis of a preparation, about a month after its separation from the alcoholic solution, showed 8.03 per cent. of ammonia, but this had not perceptibly decreased after another month.

The union of the ammonia with the dextrose molecule seems to protect it against certain general reactions, or at least delay them until the ammonia has been displaced, as the following observations will show: A carefully prepared fermentation-experiment, in which some pure dextrose was checked against the ammonia derivative, showed that while the dextrose fermented almost completely in the first twenty-four hours, the ammonia compound was quite unaffected until about thirty-six hours, and the fermentation went on slowly for more than a week. At the end of this time the degree of fermentation was practically the same as that of the pure dextrose but it was, without doubt, much less susceptible to the action of the yeast at first.

Its reducing power toward Fehling's solution was also studied: In 1-per cent. solution, titrated into undiluted Fehling's solution, 5.7 mgrs. of the substance were required to precipitate all of the copper from 1 cc. of the solution. This is appreciably less than the reducing power of dextrose, which is 4.753 mgrs. to one cc. of Fehling's solution. It was also noticeable that a longer period of boiling was necessary than under the ordinary conditions. This shows that the dextrose molecule is regenerated from the ammonia compound by the action of the alkali, and then behaves toward the Fehling's solution in the ordinary way.

It was of especial interest to study the behavior of this compound toward phenylhydrazine, which gives such characteristic products with dextrose. Upon treating 0.5 gram of the substance with phenylhydrazine chloride and sodium acetate in the manner prescribed for the preparation of dextrosazone,

no reaction occurred at 60° , and only after heating for some time at 100° did the characteristic yellow precipitate appear. This is in marked contrast with dextrose, which reacts readily at from 80° to 90° in a short time. The reaction of dextrose with phenylhydrazine in the cold, by which dextrose-phenylhydrazine is formed, was also studied: Equal parts of the ammonia compound, of water, and of phenylhydrazine were mixed and kept at ordinary temperature for ten days or more without perceptible reaction taking place. A corresponding preparation with pure dextrose gave the characteristic crystalline compound within four days. Here it is noticeable that, in the absence of sufficient heat to decompose the compound, the aldehyde group was protected against the action of the phenylhydrazine to which it is usually so susceptible.

By the action of hydrogen sulphide upon the aldehyde-ammonia compounds, are produced the *thialdines*. A study of this reaction, as applied to the dextrose-ammonia derivative, indicates that a sulphur compound is also formed, but no definite conclusions have yet been formed as to its exact nature. A watery solution of the substance was saturated with hydrogen sulphide, and on being allowed slowly to evaporate in the air a small quantity of needle-shaped crystals were observed. Some of the original alcoholic solution of the compound, before it had begun to crystallize, was also saturated with hydrogen sulphide, and after standing twenty-four hours there had separated out a granular, pale yellow precipitate. On exposure to the air and evaporation of the ammonia the yellow color of the solution disappeared and needle-shaped crystals were formed. These crystals were soft and flexible and easily melted. The material had an intensely disagreeable odor, and, on burning, gave off sulphur dioxide. When introduced into boiling Fehling's solution there was an immediate precipitation of cupric sulphide, but no reduction of copper was noted. The compound was wholly soluble in water but insoluble in alcohol, ether, and carbon disulphide. A determination of sulphur yielded over 30 per cent., but as the material was not pure this has not much significance.

An attempt was made to form salts which would seem possible from the basic nature of the compound. It is possi-

ble that the precipitates from alcoholic solution already mentioned as formed by the action of carbonic acid and hydrochloric acid were of this nature, but they also evidently contained ammonium salts of these acids also. A watery solution, to which had been added an excess of strong alcohol gave no precipitate with hydrochloric acid. Upon adding to this an alcoholic solution of platinic chloride, an immediate precipitate was formed, but this, upon separation and analysis, proved to be ammonio-platinic chloride. This would indicate that the compound is decomposed in the presence of acids.

Aside from the interest connecting to this characteristic aldehyde-reaction for dextrose, this new compound indicates the possibility of some new derivatives of the aldose sugars which will repay study. I am at present occupied with the extension of the reaction to other related sugars, and also with the investigation of some of their derivatives.

XIII. THE CARBOHYDRATES OF THE GUM OF ACACIA DECURRENS.

BY W. E. STONE.

The so-called gums, such as gum-arabic, cherry gum, peach gum, etc., which are secreted from plants probably as the result of pathological conditions are, so far as studied, capable of conversion into the sugars of the mono-saccharide group. It is perhaps too much to say that these stand in a similar relation to the sugars as do the starches and celluloses, but at least such a relation is suggested by their easy transformation into sugars by what is apparently a breaking down of complex bodies into those more simple. In some cases the gums seem to be composed of more than one kind of such sugar-producing bodies. So, for instance, gum-arabic, obtained from various sources but understood to be from certain species of acacia, yields upon hydrolysis both arabinose and galactose. The gum exuded from the bark, as well as the fruit of the peach tree also yields upon hydrolysis both arabinose and galactose. The gum of the cherry consists chiefly of the substance from which arabinose is derived. In all of these cases the gum seems of homogeneous character and,

aside from the ash-constituents which they invariably contain, no different classes of components can be isolated from them. It is not even clear in what way these differ from the insoluble constituents of plants which yield similar sugars. For instance, all of the gums which have been well studied yield arabinose and galactose. The isomer of arabinose, xylose, is never derived from this kind of material, but only from the insoluble pentosan known as xylan. Galactan, however, is gotten indifferently from both gums and the insoluble galactan found in seed coats and similar tissues. What part these gums play in the economy of the plant is also not understood, although gumosis is thought to be either a perversion of tissue-building materials from their normal function, or a direct degeneration of tissues already formed. These bodies therefore still offer much of interest to the investigator.

Some time since I received from Professor W. T. Swingle, of the United States sub-tropical experiment station at Eustis, Florida, a sample of gum which had exuded from a specimen of the Australian black wattle, *Acacia decurrens*. The sender noted that he had never before observed gumosis in this tree, and suggested a connection between the gum and the tannin which is produced so abundantly by the tree.

The gum was in the form of transparent, amber-colored masses, which were very hard and brittle. It was slowly soluble in water at ordinary temperature, forming a mucilage. Solution occurred more rapidly if a dilute solution of caustic soda was employed. The aqueous solution was slightly acid in reaction and distinctly levo-rotatory in its effect upon polarized light. Both basic lead acetate and strong alcohol precipitated from this solution a flocculent white precipitate. These characteristics are all like those exhibited by the gums already referred to.

The gum did not melt upon heating. At from 200° to 230° it blackened, and on ignition an appreciable quantity of ash remained, which was found in one case to amount to 12.17 per cent. By means of the spectroscope, calcium, potassium, and sodium were detected in this ash, and iron and sulphuric acid were also noted.

In order to determine the character of the carbohydrates present, preliminary tests were made for pentosans and for the galactose-forming group. For pentosans, one gram of gum was distilled with 100 cc. of hydrochloric acid of 1.06 specific gravity. In this distillate the furfural was determined by precipitation with phenylhydrazine after the method of Tollens and his pupils, except that the precipitate was collected and treated according to the suggestion of Krug. The yield of furfural was 25.42 per cent. (Tollens and Flint by practically the same method obtained 25.41 per cent. furfural from cherry gum.)

Galactan was tested for by heating 2 grams of the gum with 60 cc. of nitric acid of 1.15 specific gravity, upon a water-bath, by which was obtained 11.39 per cent. of mucic acid which was verified by its melting-point, 213° .

These results indicated the presence in the gum of a complex carbohydrate of the galacto-araban character, already noticed in peach gum, in the seed coats of certain leguminosæ, and probably also in the coffee berry.

In order to study the products of hydrolysis more thoroughly, 80 grams of the gum were treated with 640 cc. of 2 per cent. sulphuric acid, being heated for twelve hours in a boiling water-bath. The gum became completely dissolved, but a flocculent humin-like substance was separated. After neutralizing the acid with calcium carbonate, and evaporating the solution, there remained a dark-colored, sticky syrup. This was extracted several times with boiling alcohol and these extracts on concentration finally yielded about 10 grams of impure crystals. By repeated recrystallizations from water and alcohol, three fractions of white and apparently pure sugar were obtained. The specific rotation which is the most important character in the identification of these sugars, was determined for each of the portions.

No. 1 showed strong birotation and immediately after solution this amounted to $(\alpha)_D = +150^{\circ}$. After forty-eight hours the rotation became constant and was found to be $(\alpha)_D = +102.8^{\circ}$. This sugar reduced Fehling's solution strongly, and its osazone melted at 158° . These results agree with the constants for arabinose, which this sugar was without doubt.

No. 2 showed a specific rotation after two days of $(\alpha)_D = +86.6^\circ$. After recrystallization, by which a portion of the mother-liquor was lost, the rotation was $(\alpha)_D = +95^\circ$.

A third portion of crystals showed a rotation of $(\alpha)_D = +98^\circ$. These second and third portions were evidently mixtures of arabinose and some sugar of a lower specific rotation. In recrystallizing, it seems that the arabinose was the first to separate, and the other sugar, in the process of drying the crystals on porous porcelain plates, was lost in the mother-liquor. There is little or no doubt, however, that this was galactose, since the mucic acid obtained from the gum indicated the presence of such a carbohydrate in the material. The analogy of other gums of similar origin and character also speak for this conclusion. The specific rotation of No. 2 was also very nearly that of pure galactose, $(\alpha)_D = 83^\circ$.

The gum of *Acacia decurrens*, therefore, does not essentially differ from gum-arabic or peach gum, or cherry gum. It furnishes an additional example of the occurrence of a galacto-araban complex.

REVIEWS AND REPORTS.

THE RISE AND DEVELOPMENT OF ORGANIC CHEMISTRY. BY CARL SCHORLEMMER, LL. D., F. R. S., late Professor of Organic Chemistry in the Owens College, Manchester, Victoria University. Revised edition, edited by Arthur Smithells, B. Sc., Professor of Chemistry in the Yorkshire College, Leeds, Victoria University. London: Macmillan & Co., 1894. pp. 280.

Chemists everywhere will welcome the new edition of this extremely interesting and valuable book, which, in the Preface, Professor Smithells, the Editor, calls "a piece of work eminently characteristic of his (the author's) genius, disclosing at once the breadth and depth of his knowledge, and his ardent and disinterested love of what he was wont to term, with the pride of a disciple, 'our science.'" The Editor has written a biographical notice as an introduction, from which we learn that Schorlemmer's pupils and admirers "have decided to perpetuate his memory by erecting at Owens College a commodius laboratory (now approaching completion) for the prosecution of organic chemistry."

The book before us is probably the most readable book dealing with the history of chemistry now in existence, and it can be highly recommended to all students of chemistry.

Those who are already somewhat familiar with the subjects presented will find in it much that is suggestive. New light is thrown upon the chemical investigations and upon the most important theories of chemistry, so that the philosophy of the development of organic chemistry becomes clearer as one reads. The Editor tells us that "Schorlemmer's keen interest in the history of chemistry in which he had latterly made researches of considerable importance finally induced him to commence a book upon the whole subject. This, unfortunately, remained uncompleted at his death, but the portion which he had written, bringing the subject down to the end of last century, will be published shortly."

All the most important recent investigations in organic chemistry are skillfully summed up. The investigations of Emil Fischer, on the sugars; of Ladenburg, on the alkaloids; of Fischer and of Behrend and Roosen, on uric acid; of Von Baeyer, on indigo; and those of the same chemist on the constitution of benzene, are more clearly presented than anywhere else.

A few brief closing paragraphs of the book may appropriately find place here: "Organic Chemistry advances with giants' steps. About fifty years ago only twelve hydrocarbons were known, and twelve years ago this number had increased to about 200. To-day we are acquainted with more than 400, and many of them, as well as their numerous derivatives, have been carefully studied." "What would Gmelin say to-day? When writing his *Handbook* in 1827 he requested chemists to cease their discoveries that he might finish his work." To this the author appends the following foot-note: "When, in 1829, it was found that pyrouic acid and cyanuric acid were identical, Wöhler wrote to Liebig: 'Gmelin will say, Thank God, one acid less.'"

One who is inclined to be appalled by the mass of material dealt with under the head of organic chemistry, will be cheered by these words: "But in spite of the grand development of chemistry, nay, even for this reason, a survey becomes easier from day to day. The large chapters of former handbooks, treating of coloring matters, bitter principles, indifferent compounds, and other bodies, which could not otherwise be arranged in the system, and which Gerhardt called '*corps à sérier*', become shorter and shorter, and will disappear in the course of time."

I. R.

GRUNDZÜGE DER MATHEMATISCHEN CHEMIE. DR. GEORG HELM.
Leipzig: W. Engelmann, 1894. 138 pp. Price, 3 marks.

In Helm's *Outlines of Mathematical Chemistry* we have for the first time a logically arranged presentation of the beautiful

energy theory of chemical changes and chemical equilibria. The little book is essentially a modern production, for its subject-matter is up to date and its method is that of the energy theory, pure and simple. It deduces in orderly sequence the known relations of chemical phenomena, and it omits those unknown things which we call hypotheses.

The material which is introduced has been selected wisely, for no important element of the theory has been omitted; and yet the subject has been kept within proper limits by avoiding any undue elaboration of the fundamental formulas, and, above all, by a really scientific employment of the economy of expression which mathematical description affords. The mathematical means which are employed are nevertheless exceedingly simple, so that one is reminded still more forcibly than usual of the very true saying that "It is easier to learn the calculus than to understand a demonstration which avoids its use." It has certainly become impossible to read chemical theory without a working knowledge of the calculus.

The first part of Helm's book treats the conservation of energy, the conception of the store of energy of a body, the significance of energy differences, and the various forms in which quantities of energy appear. The resolution of such forms into their intensity and quantity factors is effected in the second part, and the simpler theorems of thermodynamics are derived. In the third part we find a charmingly simple exposition of the theory of the thermodynamical potential (the theory of affinity) comprising among its applications the general theory of chemical equilibrium, the physical theory of solutions, and the theory of the velocities of reactions. The fourth part concludes the subject by a comprehensive presentation (in only eleven pages!) of the Phase Rule of Gibbs.

To select for comment features of especial excellence from so original and consistent a treatise would be an extended task; to select details for unfavorable criticism would be a thankless one. It should, however, be stated that the author, by reason of his standing as an energy theorist, is peculiarly fitted to write such a work; nothing but good is to be said of it, and it is probably true that no existing publication is so well adapted to serve as an introduction to Physical Chemistry, as an introduction to the study of chemistry as an exact science.

J. E. TREVOR.

DIE PRAXIS DES ORGANISCHEN CHEMIKERS. DR. LUDWIG GATTERMANN, A. O. Professor an der Universität Heidelberg. Mit zahlreichen Abbildungen im Text. Leipzig: Veit & Co., 1894. pp. 303. Price, 6 marks.

This is a thoroughly practical book written by one who is a skilled experimenter and who has had much experience in

teaching organic chemistry to students in one of the busiest laboratories of the world. It differs from the much-used "Anleitung" of Emil Fischer and that of S. Levy in that it contains directions for carrying out the different kinds of operations that are necessary in organic work, such as crystallization, sublimation, distillation, extraction, drying, filtration, heating under pressure, determination of melting-points and of boiling-points. These operations are described in detail and many valuable "tricks of the trade" are presented in a thoroughly clear manner. Under the head of analytical methods are given in detail the methods in use in the best laboratories, and these are so clearly described that "he who runs may read."

The "Spezieller Teil" of the book deals with preparations after the manner of Fischer and Levy, but the presentation of the matter is somewhat more systematic than in either of these. The author has added remarks of a general character to the description of each method of preparation, with the object of giving the student something more than the mere knowledge of how to make this or that substance. He has, in fact, given us an elementary text-book of organic chemistry with experiments in the foreground. This ought to be of great value, and ought to do much towards counteracting the deplorable tendency on the part of students, even of good students, to work mechanically while in the laboratory, and to leave all reading and thinking to be done after laboratory hours. The subdivisions of the "Spezieller Teil" are I. Aliphatic Series; II. Aromatic Series; III. Pyridine and Quinoline Series; IV. Inorganic Part. All the principal reactions of the compounds of carbon are brought under the observation of the student in such a way as to impress upon his mind their general character and applicability. To illustrate, the first reaction studied is the substitution of halogen for alcoholic hydroxyl. The first example is furnished by the preparation of bromethane, and the second by the preparation of iodoethane. Then follow six pages which deal with this reaction in a general way, many examples being cited, and peculiarities in special cases being referred to. Any intelligent student working conscientiously through the course laid out must acquire a good general knowledge of organic chemistry.

I. R.

DIE MASCHINELLEN HILFSMITTEL DER CHEMISCHEN TECHNIK. A. PARNICKE. Frankfurte, a. M.: H. Beckhold, 1894. 8 vo. 320 pp.

In this well-illustrated book the author has collected and

systematically arranged, according to their several uses, the mechanical appliances usually found in large or small chemical works. Some special forms of apparatus, which may be regarded as trade secrets, are omitted, as is also apparatus of but limited application in the arts. A notable omission is the machinery used in textile coloring and printing, and the modern forms of ice machinery do not receive their proper share of treatment.

The author begins with miscellaneous subjects connected with the fitting and use of machinery, followed by interesting chapters on the transmission of power (including electric, hydraulic, and pneumatic transmission) and on transportation appliances. Disintegrating machines and mills, mixing machines, furnaces and ovens, are next considered. The chapter on concentration and evaporation contains much of interest to the technical chemist.

The eighth chapter is devoted to appliances for the mechanical separation of substances, including extraction and fractionation. Beginning with the setting of simple sieves the author passes in regular order to shaking and revolving screens, separators, presses, centrifugal machines, filter presses, sand and vacuum filters, crystallizers, extraction and fractionation apparatus. The chapter closes with a short description of the apparatus for separating gases from each other by absorption. Considerable attention is devoted to contrivances for drying and desiccation, while another chapter discusses scales and balances, thermometers, pyrometers, manometers, and dynamometers.

Finally, abstracts from the statutes and ordinances governing the construction of industrial plants and the use of industrial appliances are given. These have been made subjects of national legislation in Germany, and are not left to the judgment of a local board of aldermen, as is too often the case in this country. The prescribed penalties for infringement or disregard of the statutes are, moreover, strictly enforced in Germany.

Though intended for the use of German readers, and treating for the most part of machinery produced by German firms, the book cannot fail to commend itself also to English and American technical chemists. The explanations of the principles involved in each piece of mechanism are satisfactorily given. The descriptions of the machines are generally clear and concise, and supplemented by excellent and abundant illustrations.

FRANK H. THORP.

A TEXT-BOOK OF ORGANIC CHEMISTRY. BY A. BERNTHSEN, PH.D., Director of the Scientific Department in the Chief Laboratory of the Baden Aniline and Alkali Manufactory, Ludwigshafen-am-Rhein, formerly Professor of Chemistry in the University of Heidelberg. Translated by George McGowan, Ph.D. Second English edition revised and extended by author and translator. London: Blackie and Son, Limited; New York: D. Van Nostrand Company, 1894. 596 pp.

In the preface to the first German edition of this book the author states that "In lecturing upon organic chemistry in the University of Heidelberg I have felt more and more each session the desirability of being able to place in the hands of my students a small text-book, of which the descriptive portion was condensed as far as practicable and yet which should be of a strictly scientific character; a book which beginning with the homologous series, should lay especial emphasis upon summarizing the characteristics of each class of compounds, and, wherever possible, upon the inductive development of the theoretical relations existing between them. The following text-book of Organic Chemistry is an attempt to fulfil these requirements." That this attempt has been attended with success may be seen from the fact that four German and two English editions have been called for within the short space of six years.

On comparing this book with the first English edition it will be seen that, while the admirable original plan of treatment outlined by the author in the quotation given above is strictly adhered to, no part of the work has been left unrevised and several chapters have been completely rewritten in accordance with our present knowledge of the subject. This applies especially to the sections dealing with stereochemical isomerism, aldoximes and ketoximes, carbohydrates, special benzene formulas, hydrogen addition-products of the phthalic acids, various dyestuffs, alkaloids, the terpenes, and camphors, as well as to those sections which deal with the determination of molecular weights by physical methods, the ketonic acids and diketones, the uric acid group, the azoles, certain naphthalene derivatives, and the quinoline and acridine groups. Certain sections of the book, like those on the sugars, the albumens, the terpenes, and physical chemistry have been revised by those who have made a special study of these subjects and whose names are familiar to all chemists through their researches.

The system of International Nomenclature agreed upon at the recent conference of chemists at Geneva has been made use of both in the text and in the index, the "official name" being generally added in brackets after the name in ordinary use.

An excellent feature of the German edition which has happily been retained in the English translation is the use of two kinds of type, so that the most important matter, either in itself or for purposes of a general review, may be readily distinguished by the reader.

The number of references given in the book, though not very large, is sufficient to call the attention of the student to points which have a particular historical value or to recent researches where space does not permit of these being given in detail. The index is very complete and is free from those errors common in the ordinary index, which are so annoying to the reader.

The book is well printed and well bound. The translation is, in general, true to the original and very clear. The book is certainly one that can be most heartily recommended to both teachers and students of organic chemistry. It is quite probable, however, that teachers of the subject will find it advisable to put a more elementary book like Remsen's Organic Chemistry into the hands of beginners in the subject.

W. R. O.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. BY HENRY W. SCHIMPF, PH.G.

This work was written with special reference to the volumetric processes of the Pharmacopoeia of the United States, for the use of pharmacists and students of pharmacy, the author's experience as a teacher having convinced him of the need of a work especially designed for this class of students. The methods appear to be well selected, and the style of the book is clear and concise.

H. N. M.

ANLEITUNG ZUR DARSTELLUNG ORGANISCHER CHEMISCHER PRÄPARATE. Handbuch der Laboratoriumstechnik, enthaltend Beschreibung der Darstellungsmethoden organischer Präparate nebst Angabe ihrer Eigenschaften und Prüfung. VON DR. HUGO ERDMANN. Stuttgart: Ferdinand Enke, 1894. 610 pp.

This book is the second volume of Bender and Erdmann's Präparatenkunde. It gives detailed instructions for making over 500 organic preparations. Dr. Erdmann says in the preface that he has carefully studied the methods of formation of all of the compounds described, and in nearly every case found it possible to improve the methods, either by simplifying them or by increasing the yield. The book is unique, without a rival. In the estimation of the present writer no chemical laboratory can afford to be without it.

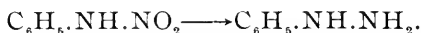
E. R.

RECENT RESEARCHES ON DIAZO-COMPOUNDS.

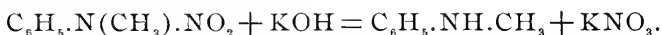
During the past two years the diazo-compounds have been the subject of many investigations, which have brought to light some important facts and led to extremely interesting speculations. In this article the attempt is made to present these results as briefly and as clearly as possible.

Bamberger has been occupied for some time with experiments on the oxidation of diazo-compounds.¹ By treating a solution of diazo-benzene with potassium ferricyanide, he obtained a compound of the formula, $C_6H_5N_2O_2K$, which he called potassium diazobenzenate (diazobenzolsaures Kalium), and from this the free diazobenzenic acid was separated. This acid Bamberger regards as phenylnitramine, $C_6H_5.NH.NO_2$, rather than phenylimidonitric acid, $C_6H_5.N:NOOH$. His reasons for holding this view are the following:

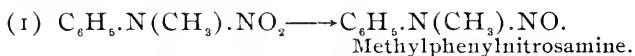
(1) Sodium amalgam reduces the compound to phenylhydrazine:



(2) The methyl ether yields methylaniline and a nitrate when treated with an alkali:



(3) The methyl ether is converted, first, into methylaniline-nitrosamine and then into methylphenylhydrazine, when treated with zinc and acetic acid:



(4) When treated with "bleaching powder" diazobenzenic acid is converted into an oily product with the general properties of the chlorimides. It is, therefore, probably $C_6H_5.N.Cl.NO_2$.

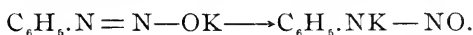
While this evidence is satisfactory as far as it goes, one fact established by Bamberger furnishes evidence in favor of the formula $C_6H_5.N=NOOH$ for diazobenzenic acid. He found that, when the silver salt of the acid is treated with methyl iodide, a methylether is obtained isomeric with that obtained when the sodium salt is used. As the latter breaks down readily into methylaniline and nitric acid, it is probably to be represented by the formula $C_6H_5.N(CH_3).NO_2$. It appears, therefore, that the former corresponds to the formula $C_6H_5.N=NOOCH_3$. Bamberger expresses the view that diazobenzene may react in two tautomeric forms. In one of these the true diazo grouping occurs, $C_6H_5.N=N.OH$. This, by oxidation, would yield the azo-compound $C_6H_5.N=NOOH$. The other

¹ See Ber. d. chem. Ges., 25, 472; 26, 482; 27, 359.

is a nitrosamine $C_6H_5 \cdot NH \cdot NO$. This, by reduction, yields phenylhydrazine.

Von Pechmann¹ has also been engaged in work on the diazo-compounds and has been led to the same general conclusions as Bamberger.

Schraube and Schmidt² further, in an article giving the results of a very thorough and skillful investigation show clearly that, in the case of paranitrodiazobenzene, two forms exist, one of which, according to the authors, is a true diazo-compound, while the other is a nitrosamine. In the course of an investigation of the transformation products of diazoparanitraniline it was observed that, when a solution of paranitrodiazobenzene chloride is added to an alkaline liquid, for example, a dilute solution of caustic soda, so that the alkali is present in excess, a clear, yellow solution is obtained, in which, although no evolution of nitrogen takes place, not a trace of a diazo-compound can be detected. From this solution crystals separate after a time, and, by neutralizing the cold solution with acid, a yellowish, difficultly soluble, crystalline precipitate is formed. Heat decomposes this with evolution of nitrogen, while, on addition of larger quantities of acid, it passes into solution; and this solution exhibits the properties of the original diazo-compound. The authors state that the crystals which separate from the alkaline solution are the sodium salt of paranitrophenylnitrosamine $C_6H_4 \cdot NO_2 \cdot NNa \cdot NO$; and the substance separated from the solution by addition of an acid is the free nitrosamine $C_6H_4 \cdot NO_2 \cdot NH \cdot NO$. The evidence offered is the same in character as that offered by Bamberger. When the sodium salt is treated with methyl iodide, the nitrosamine of nitromethylaniline $C_6H_4 \cdot NO_2 \cdot N \cdot CH_3 \cdot NO$ is formed. That the substance precipitated by acids from the alkaline solution is not free nitrodiazobenzene, $C_6H_4 \cdot NO_2 \cdot N : NOH$, but the nitrosamine $C_6H_4 \cdot NO_2 \cdot NH \cdot NO$ is shown by the fact that it gives no color-reaction when brought into an alkaline solution of β -naphthol, and, further, by the fact that, with acetic acid, it does not form the soluble acetate of the diazo-compound, and at lower temperatures it does not form easily soluble salts with mineral acids. The potassium salt of diazobenzene proved to be a true diazo-compound, but, when heated with concentrated potassium hydroxide, it is converted into the isomeric salt of phenylnitrosamine:



In a later article³ Bamberger presents an additional piece of

¹ Ber. d. chem. Ges., **24**, 3255; **25**, 3190; **25**, 3505.

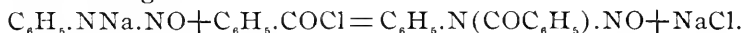
² *Ibid.*, **26**, 514.

³ *Ibid.*, **27**, 584.

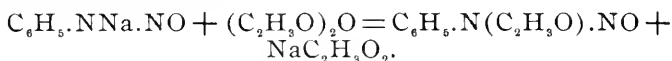
evidence in favor of the view that diazobenzenic acid has the formula $C_6H_5.NH.NO_2$, and indirectly that diazobenzene itself is a nitrosamine, $C_6H_5.NH.NO$. By treating aniline with nitrogen pentoxide he obtained diazobenzenic acid together with a number of other products. Its formation, according to Bamberger, takes place thus:

$2C_6H_5.NH_2 + N_2O_5 = 2C_6H_5.NH.NO_2 + H_2O$; a nitro-group being introduced into the anido-group.

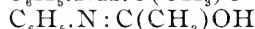
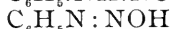
Von Pechmann and Frobenius describe¹ experiments showing that, when benzoyl chloride acts upon alkaline solutions of aromatic diazo-compounds, nitrosamines are formed in which the benzoyl is in combination with nitrogen. This reaction, according to the authors, is most easily explained on the assumption that in the alkali salts the metal is linked to the nitrogen:



Acetic anhydride acts in the same way giving acetyl derivatives of nitrosamines:



As the products thus obtained are identical with the compounds prepared by O. Fischer² by the action of nitrous acid on acid anilides, the constitution of the acetyl derivatives of the diazo-compounds is thus made clear. It follows from the above that aromatic amines, when treated successively with nitrous acid and acetic anhydride, yield identical products, independently of the order in which the reagents are applied. This indicates that the intermediate products in each case, for example, diazobenzene and acetanilide, have analogous constitutions, that is to say, that free diazobenzene is to be regarded as the anilide of nitrous acid, a conclusion already drawn by Bamberger as shown above. Further evidence in favor of this view is found in the fact that, by boiling an alkaline solution of a diazo-compound, a nitrite is formed to some extent. Assuming now that free diazobenzene is the anilide of nitrous acid, the isomeric hydroxide, $C_6H_5.N=N.OH$, appears as the analogue of the tautomeric forms of acid anilides. These are not stable in free condition, but only in the form of certain salts, for example, the imide chlorides. The following formulas exhibit the analogy:



If diazobenzene has the constitution, $C_6H_5.NH.NO$, and its alkali salts a similar constitution, nitrosamines should,

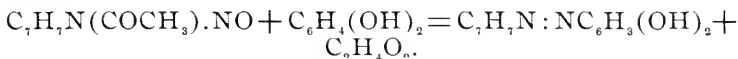
¹ Ber. d. chem. Ges., 27, 651.

² Ibid, 9, 464; 10, 959.

under proper conditions, show the reactions of alkaline solutions of diazo-compounds and, for example, give diazoamido-compounds with primary bases, and oxyazo-compounds with phenols. With nitrosanilides such reactions take place, but it is still doubtful whether they do with true nitrosamines. Thus, from nitrosoacetanilide and toluidine, diazoamidobenzene-toluene was obtained, acetic acid being split off:



This reaction can be interpreted differently. It might, for example, be supposed that the nitrosanilide is first hydrolyzed, yielding acetic acid and diazobenzene, and that the latter then acts directly upon the toluidine forming the diazoamido-compound. This explanation appears improbable to the authors, for the reason that the acetyl group is held in the nitrosanilides much more firmly than the nitroso group. The analogy between the nitrosanilides and diazobenzene is observed also in their conduct towards phenol. In both cases oxyazo-compounds are formed. The experiment was made with acetyl-*p*-tolyl nitrosamine and resorcinol, which yielded *p*-tolueneazoresorcinol and acetic acid according to the equation:



The authors claim that their experiments have furnished new evidence in favor of the view that in alkaline solution the aromatic diazo-compounds can act as nitrosamines.

Von Pechmann and Frobenius confirm¹ the statement of Schraube and Schmidt that the yellow sodium salt from *p*-nitrodiazobenzene gives with methyl iodide *p*-nitrophenyl-methylnitrosamine $\text{C}_6\text{H}_4(\text{NO}_2).\text{N}(\text{CH}_3).\text{NO}$, and they find that, when the silver salt is used instead of the sodium salt, a true ether of nitrodiazobenzene, $\text{C}_6\text{H}_4(\text{NO}_2)\text{N:NOCH}_3$, is formed. That the product has this formula appears from the following facts:

(1) When boiled with dilute acids it yields nitrogen and *p*-nitrophenol.

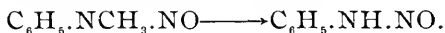
(2) When molecular quantities of the ether and of aniline are allowed to stand together for some time in alcoholic solution, yellow, silken needles of *p*-nitrodiazoamidobenzene, $\text{C}_6\text{H}_4(\text{NO}_2)\text{N:N.NHC}_6\text{H}_5$, separate.

(3) By treatment with phenol *p*-nitrobenzeneazophenol, $\text{C}_6\text{H}_4(\text{NO}_2)\text{N:NC}_6\text{H}_4\text{OH}$ is formed. The difference between the conduct of the silver salt and that of the sodium salt of *p*-nitrodiazobenzene is most easily explained by the assumption

¹ Ber. d. chem. Ges., 27, 672.

tion that the former is an oxygen salt, $C_6H_4(NO_2)N:NOAg$, and the latter a nitrogen salt, $C_6H_4(NO_2)NNa.NO$.

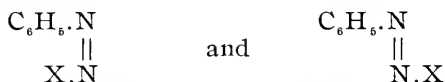
While from the above it appears that the isodiaz salts can be converted directly into nitrosamines of secondary aromatic bases, $RNH.NO \longrightarrow R.NCH_3.NO$, the reverse process had not been accomplished. This Bamberger has now done.¹ When methylanilinenitrosamine is subjected to the action of fusing potassium hydroxide the methyl group is replaced by hydrogen, while the nitroso-group, strange to say, retains its place. The product is isodiazobenzene:



Thus far everything appears clear and simple. There are two varieties of diazobenzene, the true diazobenzene $C_6H_5N=NOH$, and isodiazobenzene, $C_6H_5.NH.NO$, the latter being in fact a nitrosamine. Similar differences exist between other diazo-compounds and corresponding isodiaz-compounds. But now comes Hantzsch with the somewhat startling announcement² that the two isomeric forms of diazo-compounds are, in fact, stereoisomeric. At the beginning of his article he lays down three theses which he then proceeds to justify by reason and by experiment. These theses are:

(1) There are two structurally identical forms of diazo-compounds. Both are represented by the well-known, general structural formula, $C_6H_5.N:N.X$.

(2) (a) These two forms are stereoisomeric in the sense of the space formulas:



and are *syn-diazo-compounds* and *anti-diazo-compounds*.

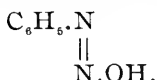
(b) The ordinary long-known diazo-compounds are *syn-diazo-compounds* corresponding to the first configuration. The isomeric diazo-compounds, which have proved to be structurally identical with these, and which are, in general, identical with the isodiaz-compounds, correspond to the second configuration. They are *anti-diazo-compounds*.

3. As regards the nature of the isodiaz-compounds the following may be remarked: There are undoubtedly isodiaz-compounds of the structural formula $C_6H_5.N:N.X$ (or $C_6H_5.N:N.OX$). But, further, the free isodiazohydrates, $C_6H_5.N_2OH$, which were discovered by Bamberger and by Schraube and Schmidt, and which they regarded as nitrosamines, $C_6H_5.NH.NO$, structurally isomeric with the true diazo-hydrates, $C_6H_5.N:N.OH$, are most probably not these

¹ Ber. d. chem. Ges., 27, 1179.

² Ibid., 27, 1702.

structurally isomeric nitrosamines, but true diazo-hydrates. They are stereoisomeric anti-diazo-hydrates



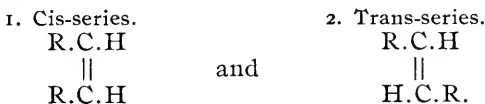
Of course, everything depends upon the evidence. Let us follow Hantzsch in his reasoning. According to the ideas first advanced by Hantzsch and Werner in regard to the stereoisomerism of compounds containing nitrogen, stereoisomerism appears probable in the case of diazo-compounds. There is a close analogy between the oximes and the diazo-compounds as is shown by the formulas :



The latter may be regarded as derived from the former by the substitution of an atom of nitrogen for the group CH. Assuming that such substitution is possible we have the following parallel series :

I. *Geometric-isomeric Carbon Compounds. General Formula,*
 $\text{R}_1\text{R}_2\text{C} : \text{CR}_3\text{R}_4.$

Simplest structural formula $\text{RHC} : \text{CHR}$ with the configurations of the



Substitution of nitrogen for CH or CR would give :

II. *Geometric-isomeric Carbon-Nitrogen Compounds. General Formula,*
 $\text{R}_1\text{R}_2\text{C} : \text{NR}_3.$

Simplest structural formula $\text{RHC} : \text{NR}$ with the configurations of the



Most important representatives :

(a) Geometric-isomeric oximes of the structural formula $\text{R}_1\text{R}_2\text{C} : \text{N.OH}$;

(b) Geometric-isomeric hydrazones of the structural formula $\text{R}_1\text{R}_2\text{C} : \text{N.NHC}_6\text{H}_5$;

(c) Geometric-isomeric imido-compounds (anils) of the structural formula $\text{R}_1\text{R}_2\text{C} : \text{N.C}_6\text{H}_5.$

A further substitution of nitrogen for CH or CR would give :

III. *Geometric-isomeric Nitrogen Compounds. General Formula,*
 $\text{R}_1\text{N} : \text{NR}_2.$

Simplest structural formula $RN:N R$ with the configurations of the

1. Syn-series.

$R.N$

\parallel

$R.N$

2. Anti-series.

$R.N$

\parallel

$N.R.$

Most important representatives:

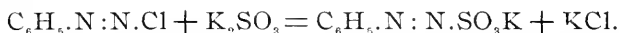
(a) Geometric-isomeric diazo-compounds of the formula $R.N:N.X$.

(b) Geometric-isomeric azo-compounds of the formula $R.N:N.R$.

The parallel between the diazo-compounds and oximes was referred to above. It appears clearest when the free oximes are compared with the free diazo-compounds in the form of hydrates; the latter appear as oximes in which nitrogen has been substituted for CH :

Structural formula of the oximes (aldoximes) $R.(CH):N.OH$;
Structural formula of the diazo-hydrates $R(N):N.OH$.

According to Hantzsch, the evidence thus far presented has failed to show that the so-called isodiazo-compounds are nitrosamines. The formation of nitrogen ethers from the alkali salts certainly does not prove the correctness of this formula, as oxygen ethers are formed from the silver salts. On the other hand Hantzsch presents what he believes to be direct evidence showing the existence of isomeric diazo-compounds, in cases in which tautomerism is out of the question. Working with F. M. Perkin he thought that they obtained two diazo-amido-benzenes which must be represented by the formulas $C_6H_5.N:N.NH.C_6H_5$ and $C_6H_5.NH.N:NC_6H_5$, and these are plainly identical, and a difference appears possible only in terms of stereochemistry. But, unfortunately for this evidence, Bamberger,¹ has since shown that Hantzsch was in error in regard to these compounds and that they are, in fact, not isomeric. Still later Hantzsch² acknowledged his error. Hantzsch has shown, further, that two salts of the formula $C_6H_5.N:N.SO_3K$ can be prepared. When a diazo salt is treated with potassium sulphite, the first product is the new isomer:



This product is darker, orange-colored, and more easily soluble than the salt hitherto known. It is unstable, indeed explosive, and, under certain conditions, it is transformed into the isomeric salt. As its most important reaction, it exhibits the characteristic property of the true diazo-compounds; it unites with phenols in alkaline solution to form azo-dyes.

¹ Ber. d. chem. Ges., **27**, 2596.

² *Ibid*, **27**, 2968.

The isomeric, secondary salt is identical with the well-known salt first described by E. Fischer. It is bright yellow, more difficultly soluble than the primary salt and more stable. The most important difference between it and the isomeric salt is seen in its conduct towards phenols with which it does not unite to form azo-dyes.

These two salts cannot be isomeric in the sense in which the two potassium salts of diazo-benzene have been supposed to be isomeric. If they were, one would have the formula $C_6H_5.N:N.SO_3K$, and the other $C_6H_5.N(SO_3K):NO$, a supposition that appears absolutely untenable in view of the fact that one of these salts is easily transformed into the other.

Bamberger replies to Hantzsch in a long article¹ which may be summed up in one sentence taken from it: "The author (Hantzsch) has not furnished a particle of evidence of the existence of isodiazo compounds $C_6H_5.N:N.X$ or $C_6H_5.N:N.OX$. Not a single fact is known, in the field of diazo-compounds, that makes it necessary to adopt the principles of stereochemistry for purposes of explanation. The stereochemical formulas of diazo- and isodiazo-compounds have decided disadvantages as compared with the ordinary structural formulas." Bamberger claims that Hantzsch has not furnished any evidence that the two sulphonates, $C_6H_5.N:N.SO_3K$, are structurally identical, and points out that they may be represented respectively by the two formulas, $C_6H_5.N:N.O.SO_3K$ and $C_6H_5.N:N.SO_3K$. Meanwhile E. Fischer had suggested this possibility to Hantzsch, and the latter attempts to show² that the view previously taken by him is the more probable. Bamberger, however, replies,³ maintaining still that the facts are far from proving that the two salts in question are stereoisomeric modifications. He admits the possibility that stereoisomerism may hereafter be observed among diazo-compounds, but holds that, at present, any assumption of stereoisomerism in this field is gratuitous.

I. R.

THE RECENT WORK OF MOISSAN UPON THE METALLIC CARBIDES.⁴

Wöhler showed that by the action of carbon on an alloy of calcium and zinc, a mixture of compounds was formed which yielded acetylene when treated with water. Lately Maquenne, following up the studies of Winkler on the reduction of the carbonates of the alkaline earths by magnesium, prepared

¹ Ber. d. chem. Ges., **27**, 2582.

² *Ibid.* **27**, 2099.

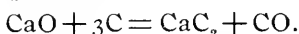
³ *Ibid.* **27**, 2930.

⁴ Bull. Soc. chim. (Paris) [3], **11**. For abstracts of former papers by Moissan dealing with research in this field, see this Journal, **15**, 374-378.

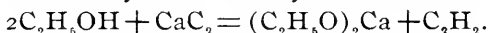
barium acetylide containing some barium hydride, which, on treatment with water, yielded acetylene mixed with 3.7 per cent. of hydrogen.

Moissan points out that while it has long been known that many fused metals can dissolve carbon, the compounds generally obtained consist of a solution of a metallic carbide in an excess of metal. To obtain definite crystallized carbides a higher heat is necessary than is obtainable in the ordinary furnace. By using his electric furnace Moissan can obtain a temperature of about 3500° , which suffices for the formation of these carbides.

If a mixture of 125 grams of quicklime with 70 grams of carbon (from sugar) is heated in a carbon crucible fifteen to twenty minutes with a current of 350 ampères and 70 volts, calcium acetylide is formed:



The yield is 120–150 grams. The acetylide is a fused black homogeneous crystalline mass of easy cleavage. Single detached crystals are opaque and lustrous. Their density is 2.22. Calcium acetylide cannot be dissolved in any acid without decomposition. It is not acted on by hydrogen. Chlorine acts at 245° forming calcium chloride and carbon; bromine acts at 350° ; iodine at 305° ; oxygen at a red heat, forming calcium carbonate; sulphur at 500° , forming calcium and carbon sulphides; phosphorus and arsenic at a red heat, forming calcium phosphide or arsenide. Dry nitrogen, silicon, and boron, do not act at any temperatures tried, up to 1200° . Few metals act: neither sodium nor magnesium attack it at the temperature at which hard glass vessels fuse; iron does not act at a red heat, but at higher temperatures forms a mixture of carbides of calcium and iron, with an alloy of calcium and iron. Dilute acids act more readily than concentrated; hydrochloric acid yields calcium chloride and acetylene. If the acetylide is heated in a tube with anhydrous alcohol, calcium ethylate and acetylene are formed:



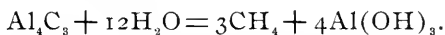
The most interesting action is that of water which at ordinary temperatures forms quantitatively acetylene and calcium hydroxide, thus furnishing the best method for the analysis of the compound.

Barium and strontium acetylides, BaC_2 and SrC_2 , have the same physical and chemical properties as the calcium salt, and were made by Moissan in the same way.

Chemists have not hitherto succeeded in making any carbides of aluminium, and some have doubted the solubility of carbon in this metal. Moissan placed carbon boats, each

filled with 15–20 grams of aluminium, in the carbon tube of his electric reverberatory furnace;¹ a current of hydrogen was then conducted through the tube and the furnace heated five minutes with a current of 300 ampères and 65 volts. The current of hydrogen was continued while the furnace was cooling. On breaking the metallic contents of the boats, the mass of aluminium was found filled with lustrous yellow crystals. The aluminium was removed by treating the mass with concentrated hydrochloric acid at low temperature. The carbide can also be formed by the action of carbon on kaoline at the same temperature. The yellow crystals are of hexagonal form, transparent and lustrous. Some were 5–6 mm. in diameter.

Aluminium carbide is more stable toward most reagents than the carbides of the alkaline earths. At a dull red heat the action was as follows: Chlorine and bromine attack it slowly; oxygen acts with extreme slowness; phosphorus and nitrogen do not act at all, but sulphur attacks it with violence, forming sulphides of aluminium and carbon. Cold concentrated hydrochloric acid acts very slowly, dilute acid more quickly. Boiling concentrated sulphuric acid is reduced to sulphur dioxide. Water at ordinary temperatures decomposes the carbide quantitatively, but very slowly, into aluminium hydroxide and methane:



The reaction—which is hastened by heat but not by light—needs ten to twelve days for completion. Still it proved the best method for analysis.

This is the first methide known, and it seems strange to rank methane with acetylene, phosphine, and hydrogen sulphide as a weak acid.

Moissan suggests that aluminium methide may play a part in the formation of the methane which is constantly escaping from fissures in the earth's crust.

The fact that all of the carbides mentioned are formed at high temperatures by the action of carbon on metal oxides, and are decomposed by water, makes it probable that the carbon now taking part in vegetable and animal life was in the form of carbides at earlier geological epochs. The calcium and aluminium carbides would have been the widest spread and most important. The decomposition of the carbides of the alkaline earths by air at a red heat, forming carbonic acid, would explain the passage of carbon from the form of a solid carbide to the gaseous form of carbon dioxide, ready for assimilation by plant life.

¹ *Compt. rend.*, **117**, 679.

In an article¹ on metallic chromium, Moissan speaks of two definite crystalline carbides of that element which he obtained by the action of carbon on chromium under varying conditions. The carbide Cr_3C_2 crystallizes in lustrous leaflets, little attacked by reagents, and not decomposed by water. The carbide Cr_4C crystallizes in lustrous needles, sometimes 1–2 cm. long. Moissan does not describe the properties of these crystals; hence the inference is that they resemble the carbide Cr_3C_2 in their stability toward reagents.

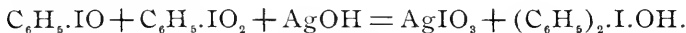
E. R.

NOTES.

Iodonium Bases.

Early last year a brief account was given in this Journal,² of some recent work by Victor Meyer and C. Hartmann on a new class of compounds containing iodine but no nitrogen. The principle substances then described were a base of the constitution, $\text{C}_6\text{H}_5 > \text{I.C}_6\text{H}_4$, and salts derived from it, such as the iodide, $\text{C}_6\text{H}_5 > \text{I.I}$, the chloride, $\text{C}_6\text{H}_5 > \text{I.Cl}$, etc. Later the authors announced³ that they had discovered a method by which they could prepare the mother-substance, of which the above-mentioned base is the moniodo substitution-product, that is to say, the compound of the constitution, $\text{C}_6\text{H}_5 > \text{I.OH}$.

This could not be prepared by the substitution of hydrogen for iodine in the base first discovered. After many preliminary experiments the following method was devised: An intimate mixture of equivalent quantities of iodosobenzene and iodobenzene is shaken with moist silver oxide, by means of a shaking machine, and then filtered. The filtrate gives with potassium iodide an abundant precipitate of the new iodide, amounting to 83 per cent. of the mixture used, that is 93 per cent. of the theoretical yield. The following equation represents the reaction:



As regards the nomenclature of the new compounds the authors remark: "The new iodide stands to iodobenzene in the same relation as *trimethylsulphonium iodide* to *methyl sulphide*, and as *tetramethylammonium iodide* to *trimethylamine*:

$\text{N}(\text{CH}_3)_3$
Trimethylamine.

$\text{HO.N}(\text{CH}_3)_4$
Tetramethylammonium hydroxide.

¹ In the same number of the *Bulletin*.

² This Journal, **16**, 233.

³ Ber. d. chem. Ges., **27**, 502.

$S(CH_3)_2$
Methyl sulphide.

$I.C_6H_5$
Iodobenzene or
phenyl iodide.

$HO.S(CH_3)_3$
Trimethylsulphonium hydroxide.

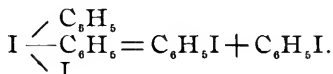
$HO.I(C_6H_5)_2$
Diphenyliodonium hydroxide.

They, therefore, call the mother-substance of the whole series, the compound $HO.IH_2$, *iodonium hydroxide* (corresponding to ammonium hydroxide, $HO.NH_4$) and designate the new iodide and hydroxide as :

$HO.I(C_6H_5)_2$
Diphenyliodonium hydroxide.

$I.I(C_6H_5)_2$
Diphenyliodonium iodide.

The new iodide crystallizes from alcohol in long yellowish needles that melt at 175° – 176° , at the same time undergoing decomposition into iodobenzene :



The free base obtained from the iodide by shaking it with moist silver oxide has a *strongly alkaline* reaction in water solution. The dilute water solutions can be kept for days without change. The chloride, $(C_6H_5)_2I.Cl$, bromide, $(C_6H_5)_2I.Br$, and pyrochromate $[(C_6H_5)_2I]_2Cr_2O_7$ are described.

The iodonium bases and their salts exhibit a marked resemblance to the derivatives of lead, silver, and especially *thallium*. The halogen compounds are precipitates which in color and solubility strongly suggest those of the metals named. The hydroxide and carbonate are soluble in water and give an alkaline reaction as in the case of thallium. This similarity raised the question whether the iodonium bases may not also give precipitates with hydrogen sulphide or ammonium sulphide. In fact, diphenyliodonium hydroxide was found to give a precipitate with ammonium sulphide looking exactly like freshly precipitated antimony sulphide.

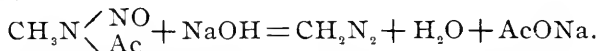
In their last article¹ on the subject of iodonium bases the authors describe the following salts in addition to those mentioned above : The nitrate, $(C_6H_5)_2I.NO_3$; the acid sulphate, $(C_6H_5)_2I.HSO_4$; the acetate, $(C_6H_5)_2I.OC_2H_3O$; the periodide, $(C_6H_5)_2I.I + I_2$; and some double salts. A further investigation of the precipitate formed by ammonium sulphide in solutions of the salts of diphenyliodonium hydroxide has shown that it consists principally of the trisulphide, $(C_6H_5)_2I.S.S.S.I(C_6H_5)_2$. This decomposes readily thus: $[(C_6H_5)_2I]_2S_3 = 2C_6H_5I + (C_6H_5)_2S_3$.

¹ Ber. d. chem. Ges., 27, 1592.

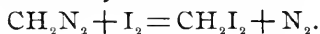
An investigation of the iodonium bases from a physiological point of view by Dr. Gottlieb, showed that their effects are similar to those produced by lead and thallium, and, in some respects, to those produced by ammonium bases. I. R.

On Diazomethane.

H. Von Pechmann¹ has succeeded in preparing the simplest conceivable organic diazo-compound, diazomethane, $\text{CH}_2\begin{smallmatrix} \diagup \text{N} \\ \diagdown \ddot{\text{N}} \end{smallmatrix}$, by treating nitrosomethylbenzoimide, nitrosomethylmethane, and other similar nitroso derivatives of methylamine with alkalies:



The product is a yellow gas. The yield is about 50 per cent. of the theoretical. While the compound at ordinary temperatures is a gas it is probably condensable by cold to a liquid. It is extremely poisonous. Owing to the difficulty of working with it the author has, for the present, confined himself to experiments with the ethereal solution. Towards acids the compound is very sensitive. The yellow ethereal solution is decolorized by them at once at ordinary temperatures with evolution of nitrogen. With iodine, diazomethane yields methylene iodide thus:



I. R.

The Composition of the Vapor of Calomel.

The determinations of the vapor-density of mercurous chloride made by Mitscherlich,² Deville and Troost,³ Rieth,⁴ and others, have all gone to show that the density found is only one-half that calculated on the basis of the formula Hg_2Cl_2 . Odling, however, called attention⁵ to the fact that calomel-vapor is capable of amalgamating gold-leaf, and Erlenmeyer⁶ was able to corroborate this statement by more conclusive experiments. An investigation by Debray,⁷ which seemed to lead to an opposite conclusion, was shown by Le Bel to be of little weight, since Debray had failed to note that at high temperatures the gold amalgam is dissociated and can, therefore, exist only for a few moments after the insertion of the cool

¹ Ber. d. chem. Ges., **27**, 1885.² Ann. der Phys. Pogg., **29**, 139.³ Compt. rend., **45**, 821.⁴ Ber. d. chem. Ges., **3**, 666.⁵ J. Chem. Soc., **3**, 211.⁶ Ann. Chem. (Liebig), **131**, 124.⁷ Compt. rend., **83**, 330.

gold-leaf into the hot vapor. The conclusion of Erlenmeyer that the decomposition $\text{Hg}_2\text{Cl}_2 = \text{Hg} + \text{HgCl}_2$, was complete, was declared by Debray, on the basis of later experiments, to be untenable, on the ground that the vapor on condensation yielded calomel as well as mercuric chloride and mercury.

The matter has, within the past year, been taken up by Victor Meyer and W. Harris, the results of whose investigation¹ are about as follows:

Gold-leaf is amalgamated by calomel-vapor at the moment of insertion, but on becoming hot returns to its original color. The temperature of vaporization of calomel is 357° . The vapor-density at 448° was found to be 8.215; at 518° , 8.169; calculated for $\text{Hg}_2\text{Cl}_2 = \text{HgCl}_2 + \text{Hg}$, 8.152. The first figure is the average of twelve, the second of eight determinations. Four experiments were made with a mixture in equivalent quantities of mercury and mercuric chloride; the average density was 8.267. In every case the residue left in the vessel, on cooling, was calomel.

On heating calomel, Meyer and Harris found that, whether a diaphragm was used or not, metallic mercury separated through its greater volatility and left a mixture of the two chlorides behind.

On inserting a stick of solid caustic potash into the vapor of calomel, an immediate deposition of mercuric oxide on its surface was noticed, precisely like that formed when the vapor is that of mercuric chloride. No deposit of mercurous oxide could be detected. To make sure that the mercuric oxide had not been formed through the decomposition of the black oxide at the temperature of the experiment, a stick of potash coated with mercurous oxide was subjected to the same temperature; the formation of mercuric oxide was not noticeable for 15–25 seconds; it then gradually changed from black to yellow. These experiments make it evident that the vapor of calomel consists of mercuric chloride and mercury, and that the mercurous salt is not volatile without decomposition. The formula of calomel must, therefore, according to Meyer and Harris be written Hg_2Cl_2 .

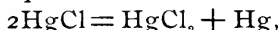
Since the publication of the paper by Meyer and Harris, M. Fileti has called attention² to an investigation, an account of which³ had been published in 1881, and in the course of which he had determined the vapor-density of calomel in the presence of the vapor of mercuric chloride. Although, according to Fileti, it was definitely proved that calomel-vapor was not dissociated under these conditions, nevertheless the density corresponded to the formula HgCl and not to the

¹ Ber. d. chem. Ges., **27**, 1482.

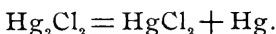
² J. prakt. Chem., [2], **50**, 222.

³ Gazz. chim. ital., **11**, 341

formula Hg_2Cl_2 . Fileti bases his view of the non-dissociation of the vapor upon the fact that a tube plated with gold and kept cool by a current of cold water, shows no sign of amalgamation on insertion into the vapor of calomel when the vaporization has been brought about in the presence of mercuric chloride as above described. Accordingly there would seem to be no reason for assuming any formula for calomel more complex than HgCl . The dissociation of calomel-vapor when heated alone should therefore, according to Fileti, be represented by the equation



and not by



Victor Meyer has since¹ replied to this paper. His answer is that Fileti's experiment is of no value as a proof of the absence of metallic mercury from the vapor of calomel when that substance is heated in the presence of mercuric chloride. On cooling the mixture of the vapors of mercury and mercuric chloride—the two substances being present in equivalent proportions—his experiments had shown that pure calomel was deposited. If now an *excess* of mercuric chloride be present, there is practically no opportunity for metallic mercury at a low enough temperature to amalgamate gold, to come in contact with the cold metal tube. The cooling of the mixed vapors would result in the formation of the two chlorides of mercury only, entirely without admixture of the metal. To test this view, a mixture of mercuric chloride and mercury in the proportion of 3 : 1, was heated and the vapor allowed to come in contact with a gold-plated copper tube kept cool by a current of cold water: no amalgamation could be noticed. Whereas, when ammonium chloride was employed instead of the mercuric salt, an immediate and most marked amalgamation was produced. All the evidence, therefore, according to Meyer, leads to the view that calomel is not volatile without complete dissociation and, since its vapor-density is that of a mixture of equivalent quantities of mercuric chloride and mercury, that its formula must be written Hg_2Cl_2 .

W. W. R.

A Sulphide of Tin Soluble in Ammonium Carbonate.

In the course of some experiments having for their object the preparation of tin absolutely free from arsenic, F. W. Schmidt² has obtained an oxysulphide of tin, which is readily soluble in ammonium sulphide. The substance can be pre-

¹ Ber. d. chem. Ges., 27, 3143.

² *Ibid*, 27, 2739.

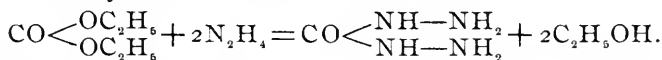
pared as follows : A solution of stannous chloride is oxidized by warming and adding nitric acid ; it is then evaporated to drive off at any rate part of the excess of acid, is diluted with water, and treated with hydrogen sulphide. The precipitated sulphide is washed, dissolved in concentrated hydrochloric acid, the solution diluted, filtered, and again treated with hydrogen sulphide, which then yields sulphide of tin free from arsenic sulphide. The precipitate is carefully washed and is then treated with a solution of ammonia ; after standing for several days at the ordinary temperature, it is practically all dissolved. After filtration the ammoniacal solution is diluted and acidified with sulphuric acid, when an almost white precipitate is thrown down. This, when freshly deposited, dissolves completely in ammonium carbonate solution. On standing it becomes less soluble. Analysis showed the dry substance to be an oxysulphide of the formula $\text{Sn}_2\text{S}_3\text{O}$. The sulphide becomes yellow in color on standing exposed to the air and at the same time less and less soluble in ammonium carbonate. Eventually it becomes insoluble ; but if the substance be redissolved in ammonia and again precipitated by addition of acid, the white voluminous sulphide is again obtained, completely soluble in the carbonate solution. The change which takes place on exposure to the air seems to be a loss of combined water and the parallel conversion of a voluminous deposit into one that is, relatively, very compact.

The bearing of this investigation upon the exact separation of the sulphides of tin and arsenic with the aid of ammonium carbonate solution, is evident.

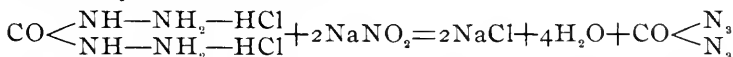
W. W. R.

Carbazide, CON_6 , and Diurea, $(\text{CO})_2(\text{NH})_4$.

The first of these interesting compounds was made by Curtius and Heidenreich¹ from carbohydrazide, a crystalline primary hydrazine, formed by the action of ethyl carbonate on hydrazine hydrate in a sealed tube at 100° :²



When the hydrochloride of this base is treated with sodium nitrite they react with ease :

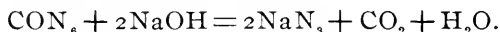


Carbazide, as first formed, is a colorless oil which explodes violently if touched ; by dissolving it in ether and allowing the ether to evaporate slowly, the carbazide is left in long crystalline needles which generally explode with violence if exposed

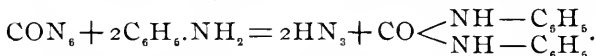
¹ Ber d. chem. Ges., 27, 2684.

² *Ibid*, 27, 56.

to light, but can sometimes be kept for a time. The substance is extremely volatile and has a penetrating and suffocating odor like that of triazoic acid or that of phosgene. It is easily soluble in alcohol or ether. Saponified with alkali, it yields a triazoate and carbonic acid:

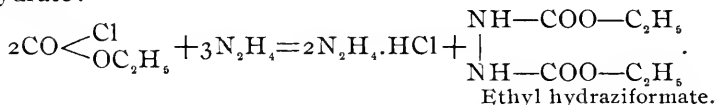


Treated with aniline it yields carbanilide and triazoic acid:

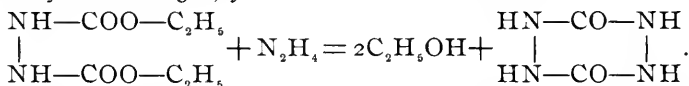


These reactions prove the constitution of the substance which may be regarded as carbonic acid in which the hydroxyl groups are replaced by triazoic-acid residues, or as triazoic acid in which the hydrogen of two molecules is replaced by the bivalent group carbonyl.

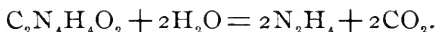
Diurea is made from ethyl hydraziformate, a crystalline salt formed by the action of ethyl chlorformate on hydrazine hydrate:¹



Ethyl hydraziformate heated in a sealed tube with hydrazine hydrate at 150°, yields diurea and alcohol:



Diurea crystallizes in monosymmetric prisms, soluble with difficulty in cold water and in alcohol. It is a strong monobasic acid, decomposing carbonates; is very stable, but can be split into hydrazine and carbon dioxide by heating with concentrated hydrochloric acid in a sealed tube at 150°:



The ammonium, barium, silver, and hydrazine salts of diurea were analyzed, as well as a benzal derivative,



which diurea forms with benzaldehyde. This benzal derivative is also a monobasic acid, as was shown by the analysis of its silver salt, $\text{C}_2\text{N}_4\text{HAgO}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_5$. E. R.

Anhydrous Hydrogen Peroxide.

Hydrogen peroxide, which is practically anhydrous, has been prepared by Richard Wolffenstein² in the organic labora-

¹ Ber d. chem. Ges., **27**, 773.

² Ber. d. chem. Ges., **27**, 3307-3312.

tory of the Technische Hochschule in Berlin. A 3-per cent. commercial solution of hydrogen peroxide was freed from all traces of alkalis, metallic sulphides, solid particles, and bodies of an indifferent chemical nature. This purified solution was concentrated on a water-bath under 68 mm. pressure to a solution containing 49.5 per cent. of hydrogen peroxide, the yield being almost quantitative. Under the ordinary atmospheric pressure a 20.2-per cent. solution was obtained, with a loss of only 12.9 per cent., when the operation took place on an oil-bath heated to 160° – 170° C. If the experiment was so conducted that the solution to be concentrated rose only to 37° C., then a 54-per cent. solution was obtained, the yield being 75.5 per cent. This method is slow, however, and it is better to evaporate the solution directly on the water-bath, care being taken that the temperature of the hydrogen peroxide solution does not rise above 75° C. This method gives a 66.6-per cent. solution, but the yield is only 28.3 per cent. When a beaker was substituted for the evaporating dish a better result followed; *viz.*, a 64.7-per cent. solution with a yield of 56 per cent. This result seemed to prove that the loss in the experiment immediately preceding the last was partly due to actual volatilization of the hydrogen peroxide and not to decomposition as has hitherto been supposed. To further substantiate this hypothesis, solutions of different strength were heated in sealed tubes to 80° C. for two hours with the following results:

9.3	per cent.-solution.	96.9	per cent.	remained	undecomposed.
47.7	"	"	82.5	"	"
48.0	"	"	74.1	"	"
68.1	"	"	74.05	"	"

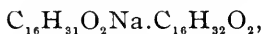
These results led the author to attempt the direct distillation of hydrogen peroxide in a vacuum. For this purpose a 45-per cent. solution was further concentrated by extraction with ether to a 73.5-per cent. solution, and the latter was distilled from a water-bath under 68 mm. pressure. The distillate was collected in two fractions, one of which boiled at 81° – 85° C. and was a 90.5-per cent. solution. This yielded by another fractionation a liquid boiling at 84° – 85° C. under 68 mm. pressure and containing 99.1 per cent. of pure hydrogen peroxide.

This is practically anhydrous hydrogen peroxide. It is a clear, sirupy liquid, which does not wet a surface as easily as water; it is volatile in the air, and is acid to litmus; when brought upon the skin, it produces a prickling sensation and white spots, which, however, disappear after a few hours. It forms two hydrates, $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$ and $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O}$, which freeze at the temperature of a mixture of solid carbon dioxide and ether.

L. C. N.

Action of Soap as a Cleansing Agent.

An explanation of the action of soap as a cleansing agent has been furnished by a recent investigation by Krafft and Stern¹. The older theory, based on the work of Chevreul, that the power of soap to dissolve fats is due to the free alkali produced by the decomposition of the salts of the fatty acids, which form the soap, has been opposed, of late, by the more modern view advanced by Rotondi (1883). According to the latter, water decomposes soap into insoluble acid salts and basic salts which remain in solution. These basic salts are the active cleansing agents. The work of Krafft and Stern confirms Chevreul's results and shows that basic salts are not formed. The action of water on the sodium salts of palmitic, stearic, oleic, and elaidic acids was studied. Sodium palmitate was boiled with varying quantities of water and the mixture which separated out on cooling was analyzed. When 900 parts of water was used the bi-palmitate,



was formed. The filtrate from the insoluble acid salt was treated with a mineral acid. Palmitic acid was not precipitated, therefore basic salts were not present. In a second experiment, when the filtrate was titrated with a standard acid, the amount of alkali found corresponded to the amount set free in the formation of the bi-palmitate. A hot solution of sodium palmitate was extracted with toluene. Pure palmitic acid was obtained. From these facts it follows that, in a hot dilute solution of sodium palmitate, a part of the salt is dissociated into free acid and free alkali. The presence of the acid in oily drops causes the cloudiness of the solution. When the solution cools, the free acid unites with some of the neutral salt to form the bi-palmitate, and the alkali remains dissolved. It is this free alkali on which the efficiency of soap depends. The action of water on the sodium salts of stearic and elaidic acids is analogous to that on the palmitate. Sodium oleate dissolves with only slight decomposition in boiling water.

J. F. N.

¹ Ber. d. chem. Ges., 27, 1747.



AMERICAN CHEMICAL JOURNAL.

ARGON, A NEW CONSTITUENT OF THE ATMOSPHERE.¹

BY LORD RAYLEIGH, SEC. R. S., AND WILLIAM RAMSAY, F. R. S., *Professor of Chemistry, University College, London.*

I. *Density of Nitrogen from Various Sources.*

In a former paper² it has been shown that nitrogen extracted from chemical compounds is about 0.5 per cent. lighter than "atmospheric nitrogen."

The mean numbers for the weights of gas contained in the globe used were as follows :

From nitric oxide.....	2.3001
From nitrous oxide.....	2.2990
From ammonium nitrite...	2.2987

while for "atmospheric nitrogen" there was found—

By hot copper (1892).....	2.3103
By hot iron (1893).....	2.3100
By ferrous hydrate (1894)•	2.3102

At the suggestion of Professor Thorpe experiments were subsequently tried with nitrogen liberated from *urea* by the action of sodium hypobromite. The hypobromite was pre-

¹ An abstract of the paper read before the Royal Society at the meeting held January 31, 1895. Communicated by the authors for publication in this Journal.

² Rayleigh: On an Anomaly encountered in Determinations of the Density of Nitrogen Gas, *Proc. Roy. Soc.*, **55**, 340 (1894).

pared from commercial materials in the proportions recommended for the analysis of urea. The reaction was well under control, and the gas could be liberated as slowly as desired.

In the first experiment the gas was submitted to no other treatment than slow passage through potash and phosphoric anhydride, but it soon became apparent that the nitrogen was contaminated. The "inert and inodorous" gas attacked vigorously the mercury of the Töpler pump, and was described as smelling like a dead rat. As to the weight, it proved to be in excess even of the weight of atmospheric nitrogen.

The corrosion of the mercury and the evil smell were, in a great degree, obviated by passing the gas over hot metals. For the fillings of June 6, 9, and 13 the gas passed through a short length of tube containing copper in the form of fine wire heated by a flat Bunsen burner, then through the furnace over red-hot iron, and back over copper oxide. On June 19 the furnace tubes were omitted, the gas being treated with the red-hot copper only. The mean result, reduced so as to correspond with those above quoted, is 2.2985.

Without using heat, it has not been found possible to prevent the corrosion of the mercury. Even when no urea is employed, and air simply bubbled through the hypobromite solution, is allowed to pass with constant shaking over mercury contained in a U tube, the surface of the metal was soon fouled.

Although the results relating to urea nitrogen are interesting for comparison with that obtained from other nitrogen compounds, the original object was not attained on account of the necessity of retaining the treatment with hot metals. We have found, however, that nitrogen from ammonium nitrite may be prepared without the employment of hot tubes whose weight agrees with that above quoted. It is true that the gas smells slightly of ammonia, easily removable by sulphuric acid, and apparently also of oxides of nitrogen. The mean result from three fillings is 2.2987.

It will be seen that, in spite of the slight nitrous smell, there is no appreciable difference in the densities of gas pre-

pared from ammonium nitrite with and without the treatment by hot metals. The result is interesting as showing that the agreement of numbers obtained for chemical nitrogen does not depend upon the use of a red heat in the process of purification.

The five results obtained in more or less distinct ways for chemical nitrogen stand thus :

From nitric oxide.....	2.3001
From nitrous oxide.....	2.2990
From ammonium nitrite purified at a red heat.	2.2987
From urea.....	2.2985
From ammonium nitrite purified in the cold.	2.2987
	<hr/>
Mean.....	2.2990

These numbers, as well as those above quoted for "atmospheric nitrogen," are subject to a deduction of 0.0006 for the shrinkage of the globe when exhausted.¹ If they are then multiplied in the ratio of 2.3108 : 1.2572, they will express the weights of the gas in grams per liter. Thus, as regards the mean numbers, we find as the weight per liter under standard conditions of chemical nitrogen 1.2505, that of atmospheric nitrogen being 1.2572.

It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have $N_2 : O_2 = 2.2984 : 2.6276 = 0.87471$; so that if $O_2 = 16$, $N_2 = 13.9954$. Thus, when the comparison is with chemical nitrogen, the ratio is very nearly that of 16 : 14; but if "atmospheric nitrogen" be substituted, the ratio of small integers is widely departed from.

To the above list may be added nitrogen prepared in yet another manner, whose weight has been determined subsequently to the isolation of the new dense constituent of the atmosphere. In this case nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by action of water upon the magnesium nitride and afterwards liberated in the free state by means of calcium hypochlorite. The purification

¹ Rayleigh : On the Densities of the Principal Gases, Proc. Roy. Soc., **53**, 134 (1893).

was conducted in the usual way, and included passage over red-hot copper and copper oxide. The following was the result:

Globe empty, Oct. 30, Nov. 5.....	2.82313
Globe full, Oct. 31.....	0.52395

Weight of gas.....	2.29918
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It differs inappreciably from the mean of other results; *viz.*, 2.2990, and is of special interest as relating to gas which, at one stage of its history, formed part of the atmosphere.

Another determination, with a different apparatus, of the density of "chemical" nitrogen from the same source, magnesium nitride, which had been prepared by passing "atmospheric" nitrogen over ignited magnesium, may here be recorded. The sample differed from that previously mentioned, inasmuch as it had not been subjected to treatment with red-hot copper. After treating the nitride with water, the resulting ammonia was distilled off, and collected in hydrochloric acid; the solution was evaporated by degrees, the dry ammonium chloride was dissolved in water, and its concentrated solution added to a freshly-prepared solution of sodium hypobromite. The nitrogen was collected in a gas-holder over water which had previously been boiled, so as, at all events partially to expel air. The nitrogen passed into the vacuum globe through a solution of potassium hydroxide, and through two drying-tubes, one containing soda-lime, and the other phosphoric anhydride.

At 18.38° and 754.4 mm. pressure, 162.843 cc. of this nitrogen weighed 0.18963 gram. Hence,

Weight of 1 liter at 0° and 760 mm. pressure = 1.2521 gram.

The mean result of the weight of 1 liter of "chemical" nitrogen has been found to equal 1.2505. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses the usual density.

Experiments were also made, which had for their object to prove that the ammonia produced from the magnesium nitride is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose the ammo-

nia was converted into ammonium chloride, and the percentage of chlorine determined by titration with a solution of silver nitrate which had been standardized by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that 1 cc. precipitated the chlorine from 0.001701 gram of ammonium chloride.

1. Ammonium chloride from orange-colored sample of magnesium nitride contained 66.35 per cent. of chlorine.

2. Ammonium chloride from blackish magnesium nitride contained 66.35 per cent. of chlorine.

3. Ammonium chloride from nitride containing a large amount of unattacked magnesium contained 66.30 per cent. of chlorine.

Taking for the atomic weights of hydrogen $H = 1.0032$, of nitrogen $N = 14.04$, and of chlorine $Cl = 35.46$, the theoretical amount of chlorine in ammonium chloride is 66.27 per cent.

From these results—that nitrogen prepared from magnesium nitride, obtained by passing “atmospheric” nitrogen over red-hot magnesium has the density of “chemical” nitrogen, and that ammonium chloride, prepared from magnesium nitride, contains practically the same percentage of chlorine as pure ammonium chloride—it may be concluded that red-hot magnesium withdraws from “atmospheric nitrogen” no substance other than nitrogen capable of forming a basic compound with hydrogen.

II. Reasons for Suspecting a Hitherto Undiscovered Constituent in Air.

When the discrepancy of weights was first encountered, attempts were naturally made to explain it by contamination with known impurities. Of these, the most likely appeared to be hydrogen, present in the lighter gas in spite of the passage over red-hot cupric oxide. But inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned, and finally it became clear that the difference could not be accounted for by the presence of any known impurity. At this stage it

seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules N_2 into detached atoms. In order to test this suggestion both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behavior of nitrogen is such as to suggest that dissociated atoms would possess a high degree of activity, and that even though they might be formed in the first instance their life would probably be short. On standing they might be expected to disappear, in partial analogy with the known behavior of ozone. With this idea in view, a sample of chemically prepared nitrogen was stored for eight months. But at the end of this time the density showed no sign of increase, remaining exactly as at first.¹

Regarding it as established that one or other of the gases must be a mixture, containing, as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of Stas and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, 0.5 per cent. only by volume would be needed; or, if the density were but half as much again as that of nitrogen, then 1 per cent. would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected.

¹ Proc. Roy. Soc., **55**, 344, 1894.

The method of most universal application by which to test whether a gas is pure or a mixture of components of different densities is that of diffusion. By this means Graham succeeded in effecting a partial separation of the nitrogen and oxygen of the air, in spite of the comparatively small difference of densities. If the atmosphere contain an unknown gas of anything like the density supposed, it should be possible to prove the fact by operations conducted upon air which had undergone atmolysis. This experiment, although in view from the first, was not executed until a later stage of the inquiry (VI), when results were obtained sufficient of themselves to prove that the atmosphere contains a previously unknown gas.

But although the method of diffusion was capable of deciding the main, or at any rate the first question, it held out no prospect of isolating the new constituent of the atmosphere, and we, therefore, turned our attention, in the first instance, to the consideration of methods more strictly chemical. And here the question forced itself upon us as to what really was the evidence in favor of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

The identification of "phlogisticated air" with the constituent of nitric acid, is due to Cavendish, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U tube.¹

Attempts to repeat Cavendish's experiment in Cavendish's manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length.

"As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmos-

¹ Experiments on Air: Phil. Trans., 75, 372, 1785.

phere, than that it is not diminished by lime-water, caustic alkalies, or nitrous air; that it is unfit to support fire, or maintain life in animals; and that its specific gravity is not much less than that of common air; so that though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties, and consequently, though it was reasonable to suppose, that part, at least, of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it was fairly to be doubted whether the whole is of this kind, or whether there are not, in reality, many different substances compounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest, which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet as some remained unabsorbed it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompose as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it, and continued the spark until no further diminution took place. Having, by these means, condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air, after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole."

Although Cavendish was satisfied with his result, and does not decide whether the small residue was genuine, our experiments about to be related render it not improbable that his residue was really of a different kind from the main bulk of

the "phlogisticated air," and contained the gas now called argon.

Cavendish gives data¹ from which it is possible to determine the rate of absorption of the mixed gases in his experiment. This was about 1 cc. per hour, of which two-fifths would be nitrogen.

III. *Methods of Causing Free Nitrogen to Combine.*

To eliminate nitrogen from air, in order to ascertain whether any other gas could be detected, involves the use of some absorbent. The elements which have been found to combine directly with nitrogen are boron, silicon, titanium, lithium, strontium, barium, magnesium, aluminium, mercury, and, under the influence of an electric discharge, hydrogen in presence of acid, and oxygen in presence of alkali. Besides these, a mixture of barium carbonate and carbon at a high temperature is known to be effective. Of those tried, magnesium, in the form of turnings, was found to be the best. When nitrogen is passed over magnesium, heated in a tube of hard glass to bright redness, combustion with incandescence begins at the end of the tube through which the gas is introduced, and proceeds regularly until all the metal has been converted into nitride. Between 7 and 8 liters of nitrogen can be absorbed in a single tube; the nitride formed is a porous, dirty orange-colored substance.

IV. *Early Experiments on Sparking Nitrogen with Oxygen in Presence of Alkali.*

In our earliest attempts to isolate the suspected gas by the method of Cavendish, we used a Ruhmkorff coil of medium size actuated by a battery of five Grove cells. The gases were contained in a test-tube standing over a large quantity of weak alkali, and the current was conveyed in wires insulated by U-shaped glass tubes passing through the liquid round the mouth of the test-tube. With the given battery and coil a somewhat short spark or arc of about 5 mm. was found to be more favorable than a longer one. When the mixed gases were in the right proportion the rate of absorption was about

¹ Phil. Trans., 78, 271 (1788).

30 cc. per hour, or 30 times as fast as Cavendish could work with the electrical machine of his day.

To take an example, one experiment of this kind started with 50 cc. of air. To this, oxygen was gradually added until, oxygen being in excess, there was no perceptible contraction during an hour's sparking. The remaining gas was then transferred at the pneumatic trough to a small measuring vessel, sealed by mercury, in which the volume was found to be 1 cc. On treatment with alkaline pyrogallate, the gas shrank to 0.32 cc. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favorable proportion.

The residue was then transferred to the test-tube with an addition of another 50 cc. of air, and the whole worked up with oxygen as before. The residue was now 2.2 cc., and, after removal of oxygen, 0.76 cc.

Although it seemed almost impossible that these residues could be either nitrogen or hydrogen, some anxiety was not unnatural, seeing that the final sparking took place under somewhat abnormal conditions. The space was very restricted, and the temperature (and with it the proportion of aqueous vapor) was unduly high. But any doubts that were felt upon this score were removed by comparison-experiments in which the whole quantity of air operated on was very small. Thus, when a mixture of 5 cc. of air with 7 cc. of oxygen was sparked for one and one-fourth hours, the residue was 0.47 cc., and after removal of oxygen 0.06 cc. Several repetitions having given similar results, it became clear that the final residue did not depend upon anything that might happen when sparks passed through a greatly reduced volume, *but was in proportion to the amount of air operated upon.*

No satisfactory examination of the residue which refused to be oxidized could be made without the accumulation of a larger quantity. This, however, was difficult of attainment at the time in question. It was thought that the cause probably lay in the solubility of the gas in water, a suspicion since confirmed. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a com-

parison with the air spectrum, taken under similar conditions, proved that, at any rate, the gas was not nitrogen. At first scarcely a trace of the principal nitrogen lines could be seen, but after standing over water for an hour or two these lines became apparent.

V. Early Experiments on Withdrawal of Nitrogen from Air by Means of Red-hot Magnesium.

A preliminary experiment carried out by Mr. Percy Williams on the absorption of atmospheric nitrogen, freed from oxygen by means of red-hot copper, in which the gas was not passed over, but simply allowed to remain in contact with the metal, gave a residue of density 14.88. This result, although not conclusive, was encouraging; and an attempt was made, on a larger scale, by passing atmospheric nitrogen backwards and forwards over red-hot magnesium from one large gas-holder to another to obtain a considerable quantity of the heavier gas. In the course of ten days, about 1,500 cc. were collected and transferred gradually to a mercury gas-holder, from which the gas was passed over soda-lime, phosphoric anhydride, magnesium at a red heat, copper oxide, soda-lime, and phosphoric anhydride into a second mercury gas-holder. After some days the gas was reduced in volume to about 200 cc., and its density was found to be 16.1. After further absorption, in which the volume was still further reduced, the density of the residue was increased to 19.09.

On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction was due to the further elimination of nitrogen, the density of the remaining gas was calculated to be 20.0.

The spectrum of the gas of density 19.09, though showing nitrogen bands, showed many other lines which were not recognizable as belonging to any known element.

VI. Proof of the Presence of Argon in Air by Means of Atmolysis.

It has already (II) been suggested that if "atmospheric nitrogen" contain two gases of different densities, it should

be possible to obtain direct evidence of the fact by the method of atmolysis. The present section contains an account of carefully conducted experiments directed to this end.

The atmolyzer was prepared (after Graham) by combining a number of "churchwarden" tobacco-pipes. At first twelve pipes were used in three groups, each group including four pipes connected in series. The three groups were then connected in parallel, and placed in a large glass tube closed in such a way that a partial vacuum could be maintained in the space outside the pipes by a water-pump. One end of the combination of pipes was open to the atmosphere; the other end was connected to a bottle-aspirator, initially full of water, and so arranged as to draw about 2 per cent. of the air which entered the other end of the pipes. The gas collected was thus a very small proportion of that which leaked through the pores of the pipes, and should be relatively rich in the heavier constituents of the atmosphere. The flow of water from the aspirator could not be maintained very constant, but the rate of 2 per cent. was never much exceeded.

The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. Oxygen was removed by red-hot copper, followed by cupric oxide, ammonia by sulphuric acid, moisture and carbonic acid by potash and phosphoric anhydride.

In a total weight of approximately 2.3 grams the excess of weight of the diffused nitrogen over ordinary atmospheric nitrogen was, in four experiments, 0.0049, 0.0014, 0.0027, 0.0015.

The mean excess of the four determinations is 0.00262 gram, or, if we omit the first, which depended upon a vacuum-weighing of two months old, 0.00187 gram.

The gas from prepared air was thus, in every case, denser than from unprepared air, and to an extent much beyond the possible errors of experiment. The excess was, however, less than had been expected, and it was thought that the arrangement of the pipes could be improved. The final delivery of gas from each of the groups in parallel being so small in comparison with the whole streams concerned, it seemed possible that each group was not contributing its proper share,

and even that there might be a flow in the wrong direction at the delivery end of one or two of them. To meet this objection, the arrangement in parallel had to be abandoned, and for the remaining experiments eight pipes were connected in simple series. The porous surface, in operation, was thus reduced, but this was partly compensated for by an improved vacuum. Two experiments were made under the new conditions, in which the excess was I, 0.0037; II, 0.0033.

The excess being larger than before is doubtless due to the greater efficiency of the atmolyzing apparatus. It should be mentioned that the above recorded experiments include all that have been tried, and the conclusion seems inevitable that "atmospheric nitrogen" is a mixture, and not a simple body.

It was hoped that the concentration of the heavier constituent would be sufficient to facilitate its preparation in a pure state by the use of prepared air in substitution for ordinary air in the oxygen-apparatus. The advance of 3.5 mgms. on the 11 mgms., by which atmospheric nitrogen is heavier than chemical nitrogen, is indeed not to be despised, and the use of prepared air would be convenient if the diffusion apparatus could be set up on a large scale and be made thoroughly self-acting.

VII. *Negative Experiments to Prove that Argon is not Derived from Nitrogen from Chemical Sources.*

Although the evidence of the existence of argon in the atmosphere, derived from the comparison of densities of atmospheric and chemical nitrogen and from the diffusion experiments (VI), appeared overwhelming, we have thought it undesirable to shrink from any labor that would tend to complete the verification. With this object in view, an experiment was undertaken and carried to a conclusion on November 13, in which 3 liters of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield a residue of argon. The gas remaining at the close of the large-scale operations was worked up as usual with battery and coil until the spectrum showed only slight traces of the nitrogen lines. When cold, the residue measured 4 cc.

This was transferred, and, after treatment with alkaline pyrogallate to remove oxygen, measured 3.3 cc. If atmospheric nitrogen had been employed, the final residue should have been about 30 cc. Of the 3.3 cc. actually left, a part is accounted for by an accident, and the result of the experiment is to show that argon is not formed by sparking a mixture of oxygen and chemical nitrogen.

In a second experiment of the same kind 5,660 cc. of nitrogen from ammonium nitrite were treated with oxygen. The final residue was 3.5 cc., and was found to consist mainly of argon.

The source of the residual argon is to be sought in the water used for the manipulation of the large quantities of gas, (6 liters of nitrogen and 11 liters of oxygen) employed. When carbonic acid was collected in a similar manner and subsequently absorbed by potash, it was found to have acquired a contamination consistent with this explanation.

Negative experiments were also carried out absorbing nitrogen by means of magnesium. In one instance 3 liters of nitrogen prepared from ammonium chloride and bleaching-powder, were reduced in volume to 4.5 cc., and on sparking with oxygen its volume was further reduced to about 3 cc. The residue appeared to consist of argon. Another experiment, in which 15 liters of nitrogen from ammonium nitrite were absorbed, gave a final residue of 3.5 cc. Atmospheric nitrogen, in the latter case, would have yielded 150 cc., hence less than $\frac{1}{40}$ of the normal quantity was obtained. It should be mentioned that leakage occurred at one stage, by which perhaps 200 cc. of air entered the apparatus; and, besides, the nitrogen was collected over water from which it doubtless acquired some argon. Quantitative negative experiments of this nature are exceedingly difficult, and require a long time to carry them to a successful conclusion.

VIII. *Separation of Argon on a Large Scale.*

To prepare argon on a large scale air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion-tube, heated in a furnace, and containing copper, in order to remove all traces of oxy-

gen ; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small U tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion tube packed tightly with magnesium turnings, and heated to redness in a second furnace. From this tube it passes through a second index tube, and enters a small gas-holder capable of containing 3 or 4 liters. A single tube of magnesium will absorb from 7 to 8 liters of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 or 150 liters of atmospheric nitrogen, which may amount to 4 or 5 liters, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide ; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide ; it then passes a reservoir of about 300 cc. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed. As the amount of gas in the tubes and reservoir diminishes in volume, it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state. The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube no gas may be lost. Before ceasing to heat, the system is pumped empty, and the collected gas is restored to the gas-holder ; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen ; or, if preferred, a mercury gas-holder may be employed. The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since called attention to the flame rising from platinum terminals, which convey a high-tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.¹ The plant consists of a De Meritens alternator, actuated by a gas-engine, and the currents are transformed to a high potential by means of a Ruhmkorff or other suitable induction coil. The highest rate of absorption of the mixed gases yet attained is 3 liters per hour, about 3,000 times that of Cavendish. It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7,925 cc., and of oxygen (prepared from chlorate of potash), 9,137 cc. On the eighth and ninth days oxygen alone was added, of which about 500 cc. were consumed, while there remained about 700 cc. in the flask. Hence the proportion in which the air and oxygen combined was as 79:96. The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow. At last the yellow line disappeared, the contraction having apparently stopped for two hours. It is worthy of notice that with the removal of the nitrogen, the arc-discharge changes greatly in appearance, becoming narrower and blue rather than greenish in color.

The final treatment of the residual 700 cc. of gas was on the model of the small-scale operations already described. Oxygen or hydrogen could be supplied at pleasure from an electrolytic apparatus, but in no way could the volume be reduced below 65 cc. This residue refused oxidation, and showed no trace of the yellow line of nitrogen, even under favorable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hours' spark-

¹ Chem. News, **65**, 301, 1892.

ing with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed that about 1.5 per cent. was clearly, and about 3 per cent. was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar connected to the secondary terminals.

IX. *Density of Argon prepared by means of Oxygen.*

A first estimate of the density of argon prepared by the oxygen method was founded upon the data already recorded respecting the volume present in air, on the assumption that the accurately known densities of atmospheric and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidized except nitrogen. Thus, if

$$\begin{aligned} D &= \text{density of chemical nitrogen,} \\ D' &= \text{“ “ atmospheric nitrogen,} \\ d &= \text{“ “ argon,} \\ \alpha &= \text{proportional volume of argon in atmospheric} \\ &\quad \text{nitrogen,} \end{aligned}$$

the law of mixtures give

$$\begin{aligned} \alpha d + (1 - \alpha)D &= D', \\ \text{or } d &= D + (D' - D)/\alpha. \end{aligned}$$

In this formula $D' - D$ and α are both small, but they are known with fair accuracy. From the data already given

$$\alpha = \frac{65}{0.79 \times 7925},$$

whence if (on an arbitrary scale of reckoning) $D = 2.2990$, $D' = 2.3102$, we find $d = 3.378$. Thus if N_2 be 14, or O_2 be 16, the density of argon is 20.6.

A direct determination by weighing is desirable, but, hitherto, it has not been feasible to collect, by this means, sufficient to fill the large globe employed for other gases. A mixture of about 400 cc. of argon with pure oxygen, however, gave the weight 2.7315, 0.1045 in excess of the weight of oxygen; viz., 2.6270. Thus, if α be the ratio of the volume of argon to the whole volume, the number for argon will be

$$2.6270 + 0.1045/\alpha.$$

The value of α , being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave $\alpha = 0.1845$; whence for the weight of the gas we get 3.193, so that, if $O_2 = 16$, the density of the gas would be 19.45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19.7, which may be taken as the density of pure argon resulting from this determination.

X. *Density of Argon prepared by means of Magnesium.*

The density of the original sample of argon prepared has already been mentioned. It was 19.09; and, after sparking with oxygen, it was calculated to be 20.0. The most reliable results of a number of determinations give it as 19.90. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density 19.90 showed no spectrum of nitrogen when examined in a vacuum-tube. It is right, however, to remark that the highest density registered was 20.38. But there is some reason here to distrust the weighing of the vacuous globe.

XI. *Spectrum of Argon.*

The spectrum of argon, seen in a vacuum-tube of about 3 mm. pressure, consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas, when examined in this way. Mr. Crookes, who will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines, as well as of some others next to be described; they are respectively 696.56 and 705.64, 10^{-6} mm.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603.84. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wave-length 561.00. There is next a blue or blue-violet line of wave-length 470.2; and last, in the

less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420.0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar-discharge is passed through argon at atmospheric pressure. The spectrum seen under these conditions has been examined by Professor Schuster. The most characteristic lines are, perhaps, those in the neighborhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water vapor. The approximate wave-lengths are

487.91	Strong.
[486.07]	F.
484.71	Not quite so strong.
480.52	Strong.
476.50	} Fairly strong characteristic triplet.
473.53	
472.56	

It is necessary to anticipate Mr. Crookes' communication, and to state that when the current is passed from the induction-coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative pole of a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. Baly,¹ who has noticed a similar phenomenon, attributes it to the presence of two gases. He says: "When an electric current is passed through a mixture of two gases, one is separated from the other and appears in the negative glow." The conclusion would follow that what we have termed "argon" is, in reality, a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the discharge has been passed for four hours, the spectrum of nitrogen disappears,

¹ Proc. Phys. Soc., 1893, p. 147.

and the argon spectrum manifests itself in full purity. A specially constructed tube, with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen, it is true; but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking the air-nitrogen with oxygen in presence of caustic-soda solution.

Professor Schuster also has found the principal lines identical in the spectra of the two gases, as observed by the jar-discharge at atmospheric pressure.

XII. *Solubility of Argon in Water.*

Determinations of the solubility, in water, of argon prepared by sparking, gave 3.94 volumes per 100 of water at 12°. The solubility of gas prepared by means of magnesium was found to be 4.05 volumes per 100 at 13.9°. The gas is, therefore, about $2\frac{1}{2}$ times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain-water. Experiment has confirmed this anticipation. "Nitrogen" prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions. The weights, corresponding to those recorded in Section I, were 2.3221 and 2.3227, showing an excess of 24 mgms. above the weight of true nitrogen. Since the corresponding excess for "atmospheric nitrogen" is 11 mgms., we conclude that the water "nitrogen" is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbonic acid, whose weight was only about midway between that of true and atmospheric nitrogen.

XIII. *Behavior at Low Temperatures.*¹

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of -90° , failed. No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon. His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical temperature (-121°) and a lower boiling-point (-187°) than oxygen, and that he has succeeded in solidifying argon to white crystals, melting at -189.6° . The density of the liquid is approximately 1.5, that of oxygen being 1.124, and of nitrogen 0.885. The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium. It showed no trace of nitrogen when examined in a vacuum-tube.

XIV. *Ratio of Specific Heats.*

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that, from the velocity of sound in a gas, the ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation

$$n\lambda = v = \sqrt{\left\{ \frac{e}{d} (1 + \alpha t) \frac{C_p}{C_v} \right\}},$$

when n is the frequency, λ the wave-length of sound, v its velocity, e the isothermal elasticity, d the density, $(1 + \alpha t)$ the temperature correction, C_p the specific heat at constant pressure, and C_v that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, and in using the same sound, many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by means of the proportion

$$\lambda^2 d : \lambda'^2 d' :: 1.41 : x,$$

¹ The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

where, for example, λ and d refer to air, of which the ratio is 1.41, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about 2 mm. diameter, and one in one of 8 mm., made with entirely different samples of gas, gave, the first, 1.65 as the ratio, and the second, 1.61.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio 1.276, instead of 1.288, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be 73.6, instead of 74.5, the mean of those previously found. The ratio of the specific heats of hydrogen found was 1.39, instead of 1.402.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, *viz.*, 1.66, proper to a gas in which all the energy is translational. The only other gas which has been found to behave similarly is mercury gas, at a high temperature.¹

XV. Attempts to Induce Chemical Combination.

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here, that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali, also when sparked; nor with chlorine dry or moist, when sparked; nor with phosphorus at a bright-red heat, nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic lustre remaining unchanged. It is unabsorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness; it passes unaffected over fused and bright red-hot potassium nitrate; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red heat. Platinum black does not absorb it, nor does platinum sponge; and wet oxidizing and chlorinating agents, such as nitrohydrochloric acid, bromine-water, bromine and alkali, and

¹ Kundt and Warburg: *Ann. der Phys. Pogg.*, **135**, 337, 527.

hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica, and of sodium and boracic anhydride, are also without action; hence, it appears to resist attack by nascent silicon and by nascent boron.

XVI. *General Conclusions.*

It remains, finally, to discuss the probable nature of the gas, or mixture of gases, which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

The presence of argon in the atmosphere is proved by many lines of evidence.

First. The high density of "atmospheric nitrogen," the lower density of nitrogen from chemical sources, and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density 20, compared with hydrogen, "atmospheric" nitrogen should contain of it approximately 1 per cent. This is, in fact, found to be the case. Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

Second. This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases, relatively to nitrogen, the amount of argon in that portion which does not pass through the porous walls. This has been proved by its increase in density.

Third. As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen, should, after the removal of the oxygen, be higher than that of "atmospheric" nitrogen. Experiment has shown that the density is considerably increased.

Fourth. It is in the highest degree improbable that two processes, so different from each other, should manufacture

the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an "atmospheric" mixture. Moreover, as argon is an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence argon cannot have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

Argon is an element, or a mixture of elements, for Clausius has shown that if K be the energy of translatory motion of the molecules of a gas, and H their whole kinetic energy, then

$$\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v},$$

C_p and C_v denoting, as usual, the specific heat at constant pressure and at constant volume, respectively. Hence if, as for mercury-vapor and for argon (XIV), the ratio of specific heats $C_p : C_v$ be $1\frac{2}{3}$, it follows that $K = H$, or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury the absence of interatomic energy is regarded as proof of the monatomic character of the vapor, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion exceedingly improbable in itself and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture

of elements; and hence it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately 20, hence its molecular weight must be 40. But its molecule is identical with its atom; hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be 40.

There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. Crookes' observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling, that in our future experimental work we shall endeavor to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have therefore to discuss the relations to other elements of an element of atomic weight 40. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between 19, that of fluorine, and 23, that of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near 40 are

Chlorine	35.5
Potassium	39.1
Calcium	40.0
Scandium	44.0

There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium, and boron, and that they are in

almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming 37 (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and 40 the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, 80, and rubidium, 85.5, *viz.*, 82, the mixture should consist of 93.3 per cent. of the lighter, and 6.7 per cent. of the heavier element. But it appears improbable that such a high percentage as 6.7 of a heavier element should have escaped detection during liquefaction.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contain



might be expected to end with an element of monatomic molecules, of no valency, *i. e.*, incapable of forming a compound, or, if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be perhaps excused, if they, in any way, lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and

comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kellas, and Matthews, who have materially assisted us in the prosecution of this research.

ON THE SPECTRA OF ARGON.¹

BY WILLIAM CROOKES, F.R.S., &c.

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train. The results are both interesting and important, and entirely corroborate the conclusions arrived at by the discoverers of argon.

The results of my examination are given in a table of wavelengths, which follows, and on a map of the lines accurately drawn to scale. The map is 40 feet long, and the probable error of position of any line on it is not greater than 1 mm.

Argon resembles nitrogen in that it gives two distinct spectra according to the strength of the induction-current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and, however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, soon disap-

¹ Read at the meeting of the Royal Society held January 31, 1895. Communicated for publication in this Journal.

pear when the induction-spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum-tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end. I have also used a Plücker tube made entirely of quartz worked before the oxyhydrogen blowpipe. I have not yet succeeded in melting platinum or iridioplatinum wire terminals into the quartz, as they melt too easily, but a very good spectrum is obtained by coating the bulbs outside with tin-foil, connected with the terminals of the induction-coil.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 mm. At this point the color of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696.56 and 705.64. On passing the current the traces of nitrogen bands soon disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs, owing to what I have called "electrical evaporation,"¹ and I think the residual nitrogen is absorbed by the finely-divided metal. Similar absorptions are frequently noticed by those who work much with vacuum-tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the color of the luminous discharge changes from red to a rich steel-blue, and the spectrum shows an almost entirely different set of lines. The two spectra, called, for brevity, red and blue, are shown on the large map, the upper spectrum being that of "blue" argon, and the lower one that of "red" argon. It is not easy to obtain the blue color and spectrum entirely free from the red. The red is easily got by using a large coil² actuated with a current of 3 ampères and 6 volts. There is then no tendency for it to turn blue. The blue color may be obtained with the large coil by actuating it with a current of 3.84 ampères and 11 volts, in-

¹ Proc. Roy. Soc., 50, 88, June, 1891.

² The coil used has about 60 miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove's cells.

tercalating a jar of 50 square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. With the small coil a very good blue color can be obtained by using 3 Grove's cells and a Leyden jar of 120 square inches surface, and a very rapid make-and-break. It appears that a low electromotive force (3 cm. spark, or 27,600 volts) is required to bring out the red, and a high E.M.F and a very hot spark for the blue. I have occasionally had an argon tube in so sensitive a state, that with the commutator turned one way the color was red, and the other way blue. Induction-coils actuated by a continuous current are never symmetrical as regards the polarity of the induced current, and any little irregularity in the metallic terminals of the vacuum-tube also acts as a valve. The red glow is produced by the positive spark and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen. In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 in all. Of these 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay, I was allowed to take some vacuum-tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's sparking and a few days' rest, the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is sparked in a tube made of pure fused quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but

the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum-tube was filled with pure argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8.84 ampères and 11 volts; no jar was interposed. At a pressure of 3 mm. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until, at a pressure of about half a millimeter, flashes of blue light made their appearance. At a quarter of a millimeter the color of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

A striking instance of a change of spectrum from nitrogen to argon was shown in a tube filled with argon kindly sent me by Lord Rayleigh. He had prepared it from the atmosphere by sparking, and it was considered to contain about 3 per cent. of nitrogen. This argon was passed into an exhausted tube and then rarefied to a pressure of 75 mm. and kept on the pump. At this pressure the nitrogen conducted all the induction-current, and the spectrum showed nothing but the nitrogen bands. The pump was slowly kept going and spectrum observations were continuously taken. When the pressure fell to about 3 mm. a change came over the spectrum; the nitrogen bands disappeared, and the spectrum of argon took its place, the only contamination being a little aqueous vapor, due to my not having sufficiently dried the gas. I took photographs of the spectrum given by this tube in the two stages, one showing the pure nitrogen bands and the other the argon lines, each being compared with the spectrum of argon prepared by Professor Ramsay. From these it is seen that the spectra given by argon, obtained by totally distinct methods from the atmosphere, are identical.

It was of interest to see how little argon could be detected in admixture with nitrogen by combined pumping and passage of the current. Some argon prepared by myself,¹ having

¹ When a current of 65 volts and 15 ampères, alternating 130 times a second, is passed through the primary of my large coil, an arching flame, consisting of burning nitrogen, issues from each of the secondary poles, meeting in the middle. When once started, the poles can be drawn asunder till the flame bridges across 212 mm. When the terminals are more than 46 mm. apart, the flame will not strike across. By enclosing this flame in a reservoir over alkaline water and feeding it with air and oxygen I can burn up a liter of air an hour.

60 to 70 per cent. of nitrogen with it, was put into a small tube furnished with large platinum terminals. Exhaustion was carried to 3 mm., and the tube was then sealed off. The spark from the large coil actuated with a current of 3.84 ampères and 11 volts was then put on, and the spectrum examined continuously. At first it was that of nitrogen bands. In about half an hour the nitrogen began to fade and the argon lines appear, and in a few minutes later the tube was just short of non-conducting. The color of the gas was rich steel-blue, and the spectrum was that of the blue argon glow. Here the small diameter of the bulbs of the tube and the large platinum wires caused much spattering or "electrical evaporation" of the platinum to take place. The pressure also is the one most suitable for that phenomenon. To this I attribute the rapid absorption of the residual nitrogen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum-tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 mm. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction-current from the large coil for eight hours before any change was noticed. The last time, when photographing its spectrum, difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The color immediately changed from the reddish-yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty, and by employing a very small jar, I was able to take one photograph of its spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through except by employing a dangerously large current. Whenever a flash passed it was of a deep blue color. Assuming that the atmos-

phre contains 1 per cent. of argon, the 3 mm. of nitrogen originally in the tube would contain 0.03 mm. of argon. After the nitrogen had been absorbed by the spattering platinum this pressure of argon would be near the point of non-conduction.

In all cases, when argon has been obtained in this manner, the spectrum has been that of the blue glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark; partly also on the degree of exhaustion. Nitrogen, when present, conducts the current easiest. As the exhaustion increases and the conductivity of the nitrogen diminishes, that of the red-glowing argon rises, until, at a pressure of about 3 mm., it is at the greatest, and the luminosity is best. Beyond that point the conductivity of the red form seems to get less, and that of the blue form to increase, till the vacuum approaches a fraction of a millimeter, when further pumping soon renders it non-conducting. It is not improbable, and I understand that independent observations have already led both the discoverers to the same conclusion, that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body, has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum-tubes containing rarefied nitrogen, which show either the fluted band or the sharp line-spectrum by simply turning the screw of the make-and-break, exactly as the two spectra of argon can be changed from one to the other.

The disappearance of the red glow and the appearance of the blue glow in argon as the exhaustion increases also resembles the disappearance of the red line of hydrogen when exhaustion is raised to a high point. Plücker, who was the first to observe this occurrence, says:¹ "When Ruhmkorff's small induction-coil was discharged through a spectral tube

¹ On the Spectra of Ignited Gases and Vapors: Plücker and Hittorf, *Phil. Trans.* **155**, 21 (1865), Part I.

enclosing hydrogen, which was gradually rarefied to the highest tenuity to be reached by means of Geissler's exhauster, finally the beautiful red color of the ignited gas became fainter, and passed gradually into an undetermined violet. When analyzed by the prism, $H\alpha$ (the red, C, line) disappeared, while $H\beta$ (the green, F, line), though fainter, remained well defined. Accordingly, light of a greater length of wave was the first extinguished."

I have prepared tubes containing other gases, as well as nitrogen at different pressures, and have examined their spectra both by eye observations and by photography. The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed will show that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at 531.7, the aurora line at 557.1, and the helium line at 587.5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapor yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. Having once obtained a tube of argon giving the pure spectra, I can make no alteration in it, except that which takes place on varying the spark or increasing the exhaustion, when the two spectra change from one to the other. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two, members to the family of elementary bodies.

The Two Spectra of Argon.

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
		764.6	2	
		750.6	4	
		737.7	3	
		726.3	2	
		705.64	10	
		696.56	9	
		684.2	2	
		675.4	6	
		666.4	6	
662.8	4			
		640.7	9	
		637.7	2	
		630.2	4	
		628.1	2	
623.2	4	621.0	6	
617.3	6	617.3	6	Coincident.
		614.3	2	
612.0	6			
		609.9	4	
		605.6	2	
		604.5	3	
603.8	8	603.8	8	Coincident.
		593.5	1	
592.6	4	592.6	4	Coincident.
		590.9	6	
		588.7	6	
		585.8	4	
		583.4	2	
		580.3	1	
		577.1	2	
		574.6	6	
		568.3	2	
		565.1	9	
		561.0	9	
		556.7	2	
		555.7	10	
		552.0	1	
		550.1	2	
		549.65	8	
		545.6	6	
		544.4	2	

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
		542.1	4	
		525.8	6	
		522.2	7	
		518.58	10	
		516.5	9	
514.0	10			
506.5	10	506.5	4	Coincident.
501.2	2	501.2	4	Coincident.
500.7	9			
496.55	9	496.55	4	Coincident.
493.8	10	493.8	2	Coincident.
487.9	10	487.9	4	Coincident.
484.75	1			
480.50	7			
476.30	1			
473.45	6			
472.66	2			
		470.12	8	
465.65	5			
		462.95	5	
460.80	8			
		459.45	2	
458.69	6			
457.95	6			
454.35	7			
		451.40	2	
450.95	8	450.95	9	Coincident.
447.83	6			
442.65	10			
442.25	10			
439.95	10			
437.65	9			
436.90	9			
434.85	10			
		434.50	5	
433.35	9	433.35	9	Coincident.
		430.05	9	
429.90	9			
427.70	3			
427.20	7	427.20	8	Coincident.
426.60	6	426.60	4	Coincident.
425.95	8	425.95	9	Coincident.
425.15	2	425.15	3	Coincident.
422.85	6			
420.10	10	420.10	10	Coincident.

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
419.80	9	419.80	9	Coincident.
419.15	9	419.15	9	Coincident.
418.30	8	418.30	8	Coincident.
416.45	8	416.45	4	Coincident.
415.95	10	415.95	10	Coincident.
		415.65	6	
413.15	3			
410.50	8			
407.25	8			
404.40	8	404.40	9	Coincident.
403.30	1			
401.30	8			
397.85	1			
396.78	3			
394.85	9	394.85	10	Coincident.
394.35	3			
393.18	3			
392.85	9			
392.75	3			
391.50	1			
		390.45	8	
389.20	5			
387.55	2			
387.18	2			
386.85	8			
385.15	10			
384.55	1			
383.55	2	383.55	3	Coincident.
382.75	2			
380.95	4			
380.35	1			
379.95	1			
378.08	9			
		377.15	1	
377.05	2			
376.60	8			
373.85	3			
372.98	10			
371.80	4			
		363.25	2	
363.17	1			
		362.37	1	
		362.28	1	
361.75	2			
360.50	3	360.50	5	Coincident.
358.70	10			

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
358.03	9			
357.50	9			
356.65	2	356.65	4	Coincident.
356.40	2			
		356.28	1	
356.00	2			
355.82	7			
355.45	4	355.45	6	Coincident.
354.75	4			
354.45	7			
353.43	4			
352.05	3			
351.92	4			
351.35	6			
350.88	4			
349.00	10			
347.57	7			
345.35	1			
338.80	1			
309.27	5			
308.48	4			
306.47	2			
304.27	3			
299.82	1			
297.86	1			
294.27	2			
292.96	1			
283.02	1			
279.44	2			
273.45	2			
270.72	0.5			
269.30	1			
266.12	2			
265.26	3			
262.95	1			
257.12	2			
256.07	1			
248.49	1			
243.85	2			
224.66	3			

119 lines in the "Blue" Spectrum.

80 lines in the "Red" Spectrum.

199 total lines.

26 lines common to the two spectra.

THE LIQUEFACTION AND SOLIDIFICATION OF ARGON.¹

BY K. OLSZEWSKI, *Professor of Chemistry in the University of Cracow.*

Having been furnished by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behavior at low temperatures and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 cc. It was contained in a hermetically sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19.9 ($H = 1$); and he thought that at the outside it might contain 1 to 2 per cent. of nitrogen, although it showed no nitrogen-spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as of measuring its vapor-pressure at several other low temperatures, while two other series served to determine its boiling and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene

¹ Read by Prof. W. Ramsay at the meeting of the Royal Society held January 31, 1895. Communicated for publication in this Journal.

had comparatively thin walls (not exceeding 1 mm.), so as to equalize the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end of the burette with a mercury-reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume, in the liquid state, measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

Determination of the Critical Constants of Argon.

As soon as the temperature of the liquid ethylene had been lowered to -128.6° , the argon easily condensed to a colorless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures:

Expt.	Temperature.	Pressure.
1	-121.2°	50.6 atmos.
2	-121.6°	50.6 "
3	-120.5°	50.6 "
4	-121.3°	50.6 "
5	-121.4°	50.6 "
6	-119.8°	50.6 "
7	-121.3°	50.6 "

In all seven determinations the critical pressure was found to be 50.6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6, less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapor-pressures of argon, a tabular record of which is given below, I noticed slight differences of

pressure according as I produced more or less of the liquid at the same temperature. This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is -121° , and this may be taken as the critical temperature of argon.

At lower temperatures the following vapor-pressures were recorded:

Expt.	Temperature.	Pressure	Expt.	Temperature.	Pressure.
8	-128.6°	38.0 atmos.	13	-134.4°	29.8 atmos.
9	-129.6°	35.8 "	14	-135.1°	29.0 "
10	-129.4°	35.8 "	15	-136.2°	27.3 "
11	-129.3°	35.8 "	16	-138.3°	25.3 "
12	-129.6°	35.8 "	17	-139.1°	23.7 "

In experiments Nos. 9, 10, and 17 the quantity of liquefied argon was very small, for it filled the tube only to a height of 3—5 mm., and in the other experiments the column of liquid argon was 20 mm. high or more.

Determination of the Boiling- and Freezing-Points.

200 cc. of liquid oxygen, prepared in my large apparatus,¹ was poured into a glass vessel with quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about 70 cc., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature (-182.7°)² on admitting argon, no appearance of liquefaction could be noticed, even when compressed by increasing the atmospheric pressure by a quarter. This shows that its boiling-point lies below that of oxygen. But on diminishing

¹ Bulletin international de l'Académie de Cracovie, June, 1890; also Beibl. Ann. der Phys., 15, 29.

² I have re-determined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is 1.3° lower than that which I previously recorded.

the temperature of the liquid oxygen below -187° , the liquefaction of the argon became manifest. When liquefaction had taken place, I carefully equalized the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers -186.7° , -186.8° , -187.0° , and -187.3° . The mean is -186.9° , which I consider to be the boiling-point under atmospheric pressure (740.5 mm.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 99.5 cc.; the quantity of liquid corresponding to that volume of gas was approximately 0.114 cc. Hence the density of argon at its boiling-point may be taken as approximately 1.5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given cannot lay claim to great exactness; yet they prove that the density of liquid argon at its boiling-point (-187°) is much higher than that of oxygen, which I have found, under similar conditions, to be 1.124.

By lowering the temperature of the oxygen to -191° by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting-point gave the numbers: -189.0° , -190.6° , -189.6° , and -189.4° . The mean of these numbers is -189.6° ; and this may be accepted as the melting-point of argon.

In the following table I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the following table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place, *viz.*, between carbon monoxide and oxygen. Its behavior on liquefaction places it nearest to oxygen, but it differs entirely from oxy-

Name.	Critical temperature.	Critical pressure.	Boiling-point.	Freezing-point.	Freezing-pressure.	Density of gas.	Density of liquid at boiling-point.	Color of liquid.
Hydrogen (H_2).....	{ Below —220.0°	Atmos. 20.0	?	?	mm. ?	1.0	?	Colorless.
Nitrogen (N_2)	—146.0°	35.0	—194.4°	—214.0°	60	14.0	0.885	"
Carbonic oxide (CO)	—139.5°	35.5	—190.0°	—207.0°	100	14.0	?	"
Argon (A_1).....	—121.0°	50.6	—187.0°	—189.6°	?	19.9	About 1.5	"
Oxygen (O_2).....	—118.8°	50.8	—182.7°	?	?	16.0	1.124	Bluish.
Nitric oxide (NO)...	— 93.5°	71.2	—153.6°	—167.0°	138	15.0	?	Colorless.
Methane (CH_4).....	— 81.8°	54.9	—164.0°	—185.8°	80	8.0	0.415	"

gen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling-point seem to have some relation to its simple molecular constitution.

ON THE ATOMIC WEIGHT OF OXYGEN. SYN-
THESIS OF WEIGHED QUANTITIES OF
WATER FROM WEIGHED QUAN-
TITIES OF HYDROGEN AND
OF OXYGEN.

BY EDWARD W. MORLEY.

Many most valuable contributions to our knowledge of the atomic weight of oxygen have been made within ten years by Rayleigh, by Dittmar and Henderson, and by Scott, in England, by Leduc in France, by Thomsen in Denmark, and by Cooke and Richards, by Keiser, and by Noyes, in this country. My own experiments began many years before I learned that others were at work on the subject; but as no assistance could be afforded me, and as, till after the completion of the experiments described in this paper, the whole expense fell upon me, the progress made was so slow that it often seemed hardly worth while to go on.

The process used by Berzelius and Dulong, and by Dumas was first studied. Perhaps the opinion unfavorable to its precision which was formed may be modified by the experience of others, but until our knowledge of the properties of cupric oxide becomes such that we can easily prepare an oxide free from everything but copper and oxygen, the process can hardly be made capable of satisfactory precision. But it cost a year to come to this decision.

It also cost much time to learn how, with ease and certainty, to prepare hydrogen of sufficient purity. When this was accomplished, the method of weighing the gas directly had to be chosen. Some of my globes had a capacity of 21.5 liters,

so that 1.8 grams of hydrogen could be weighed in one of them. Since the weight of such a globe can be determined with a mean error of less than a tenth of a milligram in a single weighing, the process is not an unpromising one. But while it is easy to prepare pure hydrogen, and easy to weigh it, it is by no means easy to introduce it into the globe without contamination, either by mercurial vapor, from a mercurial air-pump, or by organic vapors from the lubricant of a piston air-pump. The difficulties could be surmounted, if no alternative method were available. But there is a better method, and it is easy.

One method of directly weighing hydrogen is, to weigh a suitable gas-bottle with its drying train, then to generate hydrogen in it by the solution of a metal in an acid or in an alkali, and then weigh again. Some of the forms of apparatus which were tried would permit me to weigh over 4 grams of hydrogen in each experiment. But it was impossible to procure easily a metal which gave pure hydrogen, or hydrogen which could be purified with a simple purifying train. Nothing would answer my purpose except zinc redistilled in a vacuum so as to free it from carbon.

There remained only the costly recourse to the method depending on the use of palladium. Chirikoff seems first to have suggested the use of palladium as a means of purifying hydrogen. I began experimenting with the present investigation in mind in 1883, though on a small scale.

The experiments to be described in this paper consist of twelve syntheses of weighed quantities of water from weighed quantities of hydrogen and of oxygen. The hydrogen was absorbed in 600 grams of palladium; the oxygen was weighed in two globes, in the form of gas. Full details of the experiments are ready for a publication of the Smithsonian Institution, to which those are referred who care to know the nature of the apparatus used, and to see the quantities determined by the balance or the eudiometer, unmodified by any computation. The present paper is but a brief abstract of one part of that paper, giving the final results of each of the experiments, and such a general description of the apparatus as may be sufficient for many.

Apparatus for Producing and Weighing Water.

The apparatus for producing and weighing water consisted of a thin glass tube some 22 centimeters long and 25 millimeters in diameter, Figure 1. Midway in its length, were inserted two tubes, ending within in two platinum jets parallel to the axis of the tube. Just above these jets were two platinum wires for inflaming the jet of hydrogen or of oxygen. The gases came to the jets through drying tubes filled with phosphorus pentoxide, so that the uncombined gases could enter, but the water produced could not escape, if the apparatus were properly used. The ends of the drying tubes were furnished with ground-joints by which they could be joined to the apparatus for regulating the admission of the gases. The volume of the apparatus was not far from 250 cc., and the weight nearly 100 grams. Before using it, it was exhausted to the ten thousandth of an atmosphere, and closed by fusion. Its volume was determined, and it was then weighed accurately against a counterpoise of the same volume and of 35 or 40 grams greater weight.

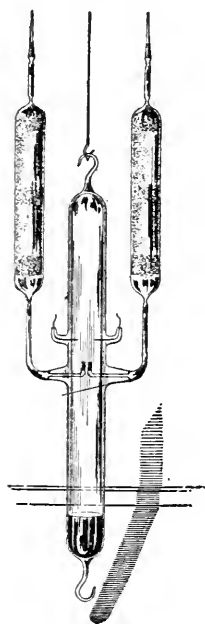


FIGURE 1.

Apparatus for Weighing Hydrogen.

My plant for weighing hydrogen contained 600 grams of palladium; in the first and second experiments this was divided between two tubes, but in the rest, it was all in one tube. Some trifling modifications of its form were made after each accident to it; all these are mentioned in the paper to be issued by the Smithsonian Institution. In the final form no stop-cock was used on this tube; but even in those experiments in which the stop-cock was still attached to the tube, it was never used for any purpose except to regulate the current of gas for a moment. A most fruitful source of annoyance, or even of serious error, was avoided by depending solely on fusion for closing this tube. The tube containing

palladium having been connected by fusion to the source of hydrogen shown at Figure 1 in my paper on the "Volumetric Composition of Water,"¹ the palladium was heated, and a current of the gas was passed for half an hour or more. The tube was then closed by fusion, the metal was cooled, and the gas was passed into it to saturation. The tube was then again opened and a current of the gas was passed for two or three hours, so as to remove any nitrogen which might conceivably have accumulated, after which it was closed by fusion at all points, its volume was determined by hydrostatic weighing, and its weight was determined by the method of reversal, using a counterpoise of the same volume and the same weight. The observations of weight were repeated at intervals.

Apparatus for Weighing Oxygen.

The two globes used for weighing oxygen contained 20.0 and 21.5 liters. They were provided with counterpoises which were equal to them in volume when the globes were exhausted, and the expansion of the globes produced by filling them with gas was compensated, the compensation being a simple and accurate method of dispensing with the observations of pressure and temperature which would have been necessary in order to compute corrections for differences of volume. The globes were exhausted with a Toepler pump to one part in thirty or fifty thousand, and filled with pure and dry oxygen. They were weighed as stated before. It was thought that the amount of mercury vapor which contaminated the oxygen was negligible, experiments seeming to justify this opinion. That the oxygen was free from chlorine, although made from potassium chlorate, was proved by suitable examination of the water produced from it.

Balance.

The balance used was made by Becker, of Rotterdam, and carries a kilogram in each pan. It was procured for this investigation, and has been used for nothing else. It was set up in a room of nearly constant temperature, on the stone

¹ Am. Jour. Science, 41, 225.

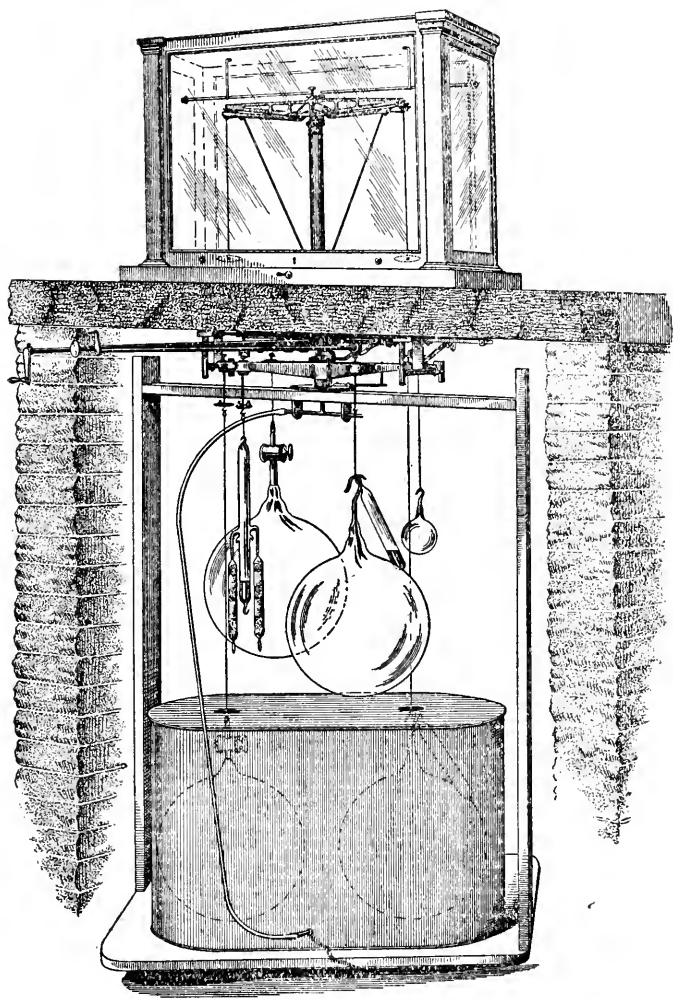


FIGURE 2.

Figure 2 shows the balance and the mechanism for weighing by reversal. The apparatus was photographed while supported temporarily for the purpose, and the drawing made from the photograph as accurately as the artist could well do it, but some details are not quite correct. Hooks attached to the pans of the balance pass down through the stone cover of the vault. Six hooks carrying the globes and other objects are supported by six arms just below the stone. By means of the handles seen well to the left, any one of these six hooks can be engaged in either of the first pair, and then left attached to it, and free from contact with the arm. The current of dry air needed to supply the desiccators was introduced through the axis of the reversal mechanism, as suggested by the rubber tube in the drawing. The desiccators for the second and third pairs of objects are not shown.

cover of a closet or cave of a little more than a meter in each internal dimension. Under the balance, fastened to the under side of this stone cover, is a reversal apparatus by means of which any one of three pairs of objects may be suspended from either pan of the balance without opening the cave or approaching the balance. With this apparatus, objects to be weighed were placed in the cave, each pair in its desiccator, and left in dry air for hours before weighing. After weighing each pair of objects at least four times, by reversal, at intervals of at least half an hour, it was hoped that the weights might be considered fairly determined. The probable errors of the results seem to justify this hope.

Combining the Gases to Produce Water.

When the hydrogen, the oxygen, and the apparatus for containing the water produced, had been weighed, the apparatus was set together. The apparatus for producing water was opened by breaking off the tubes near the ground-joints of the drying tubes, of course taking means to prevent the admission of moisture with the entering air. The apparatus was then connected to the system of stop-cocks and gauges for controlling the admission of the gases. To this same system were then connected the palladium tube and the two globes of oxygen. Before these were opened to admit gases to the system, the combustion apparatus and the system of tubes were exhausted by a Toepler pump which was permanently connected to the apparatus. After the pump was shut off, the gases were admitted to the connecting tubes and into the combustion apparatus itself where they were ignited by sparks between the wires for the purpose. Immersion in water kept this part of the apparatus at a suitable temperature.

After the combustion was ended, the palladium tube and the globes for oxygen were closed, and the water which had been produced was cooled to -20° , so as to make the tension of its vapor small. The Toepler pump again exhausted the apparatus, and the gas withdrawn from the globes and the tube of palladium, but remaining unconsumed in the apparatus, was transferred to an eudiometer. The combustion

apparatus was closed by fusion and weighed together with the parts removed in the manipulation of opening and closing it. The same was done with the tube containing palladium, which was also weighed hydrostatically, to detect any change of volume due to heating. When the globes had been weighed, it was known how much had been withdrawn from each source of gas. The unconsumed residue being measured and analyzed, and the proper subtraction being made, it was known how much of each gas had been combined to form water, which gave the ratio sought. From the weight of water produced, compared with the weight of hydrogen used, was obtained a second determination of the ratio.

No rubber joints were used about the apparatus; all connections were made by fusion, except where parts had to have their weight preserved unchanged, when they were connected to adjoining pieces by suitable ground-joints made tight with paraffin.

The results of the twelve experiments made by this method are given in the following table.

Weights of hydrogen, of oxygen, and of water formed, with ratios deduced:

Hydrogen.	Oxygen.	Ratio.	Water.	Ratio.
3.2645	25.9176	15.878	29.1788	17.877
3.2559	25.8531	15.881	29.1052	17.878
3.8193	30.3210	15.878	34.1389	17.873
3.8450	30.5294	15.880	Apparatus broken.	
3.8382	30.4700	15.877	34.3151	17.881
3.8523	30.5818	15.877	34.4327	17.876
3.8297	30.4013	15.877	34.2284	17.875
3.8286	30.3966	15.878	34.2261	17.879
3.8225	30.3497	15.879	34.1742	17.881
3.8220	30.3479	15.881	34.1743	17.883
3.7637	29.8865	15.881	33.6540	17.883
3.8211	30.3429	15.882	34.1559	17.878

Means..... 15.8792 ± 0.00032 17.8785 ± 0.00066

Besides the full details of experiments here briefly described, the paper now in the hands of the Secretary of the Smithsonian Institution contains three series of determinations of the density of oxygen under normal conditions at the sea-level in latitude 45° ; two series of similar determinations for hydrogen by the processes hitherto used, which are

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rejected for a suspected source of error incident to such determinations; three series of determinations of the density of hydrogen by a new method which avoids the error suspected, which were carried out with two independent apparatus; and a determination of the volumetric composition of water by a process which is, in one respect, similar to that lately used by Leduc. The combination of these quantities gives a third determination of the atomic weight of oxygen, of which the trustworthiness, as far as can be judged from probable errors, is equal to that of any determination hitherto made; and it agrees absurdly well with the two results from the syntheses. In this work on the densities, I have had generous help from Mrs. Amasa Stone, from Messrs. Warner and Swasey, from Mr. C. W. Wason, from the East Cleveland Railroad Company and the succeeding corporation, the Cleveland Electric Railway Company, and from the Smithsonian Institution; which I am glad of the opportunity to acknowledge.

The following table gives the more important results of the work on the densities and volumetric composition, together with the final results of the experiments described in the present paper. To it is appended a table showing the results of previous experimenters, which Professor F. W. Clarke had revised for a forthcoming work, and which he kindly furnished to me:

Density of oxygen, latitude 45°.....	1.42895 ± 0.000034
Density of hydrogen.....	0.08987 ± 0.0000027
Ratio of densities.....	15.9002 ± 0.00061
Volumetric composition of water at 0°.	2.0027 ± 0.00014
Atomic ratio from densities and volumetric ratio.....	15.879 ± 0.0011 ¹
Atomic ratio, syntheses.....	15.8792 ± 0.00032
Molecular weight of water, syntheses..	17.8785 ± 0.00066
Results of other experimenters. Atomic ratio.	
Berzelius and Dulong.....	15.894 ± 0.057
Dumas.....	15.961 ± 0.007
Erdmann and Marchand.....	15.975 ± 0.011
Cooke and Richards.....	15.869 ± 0.0020
Keiser, 1888.....	15.951 ± 0.0011
Rayleigh, syntheses.....	15.89 ± 0.009
Noyes.....	15.897 ± 0.0017

¹ Atomic ratio, from densities and volumetric ratio by Scott's experiments 15.878.

Results of other experimenters.	Atomic ratio.
Dittmar and Henderson.....	15.867 \pm 0.0046
Leduc.....	15.881 \pm 0.013
Morley.....	15.879 \pm 0.0003

Results of other experimenters.	Ratio of densities.
Regnault, corrected by Crafts.	15.9105 \pm 0.0044
Rayleigh, 1888.....	15.884 \pm 0.0048
“ 1892.....	15.882 \pm 0.0023
Cooke.....	15.890 \pm 0.0067
Leduc.....	15.905 \pm 0.015
Morley.....	15.900 \pm 0.0006

Volumetric composition of water.

Scott.....	2.00285
Morley, eudiometer, (reduced to 0°).....	2.0008
Leduc.....	2.0038
“ corrected, according to my reduction.	2.0024

While the value 2.0002, which I obtained by direct measurement, is the value which I am certain would be obtained by others working with pure gases in an apparatus of the nature and dimensions used, it is obvious that the result is not a measurement of the quantity desired, but that it is complicated with a phenomenon which is hinted at by the fact that both my own experiments and those of Scott in an apparatus of similar dimensions, yield a result in which the volume of the oxygen comes out too large. But whether I shall have the means of elucidating the supposed cause, remains for the future. I think we may safely trust the values obtained by Scott and by myself in our last determinations ;—

Scott.....	2.00285
Morley.....	2.00270

ON THE CHLORONITRIDES OF PHOSPHORUS.¹

BY H. N. STOKES.

“Chlorophosphuret of nitrogen” (*Chlorphosphorstickstoff*) was discovered in 1832 by Liebig,² while attempting to pre-

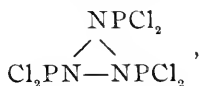
¹ The following work was begun in the laboratory of the School of Pharmacy, Northwestern University, Chicago, and continued in the laboratory of the United States Geological Survey. I wish to express my sincere thanks to Prof. J. H. Long, of the former institution, for his kindness in permitting me to work in his laboratory, and to Prof. F. W. Clarke, of the Geological Survey, for the opportunity of continuing the investigation.

² Liebig-Wöhler, Briefwechsel 1, 63; Ann. Chem. (Liebig), 11, 146, (1834).

pare amides of phosphoric acid by acting on phosphorus pentachloride with gaseous ammonia and with ammonium chloride. Analysis¹ led to the formula $P_3N_2Cl_5$, and he observed that the compound could be distilled with steam, or boiled with acids or alkalis without appreciable decomposition—properties unique in a phosphorus-chlorine compound.

Liebig did not pursue the subject much further, but at his suggestion Gladstone² in 1849 continued the study of the phosphorus-nitrogen compounds and, incidentally, of chlorophosphuret of nitrogen. In his papers on this body,³ Gladstone detailed a method of preparation from phosphorus pentachloride and ammonium chloride, and pointed out some of its properties—among them its decomposition in aqueous ether or by alcoholic alkalis, into hydrochloric acid and a nitrogenous compound, deutazophosphoric acid. Gladstone adopted Liebig's formula, $P_3N_2Cl_5$. The correctness of this was disputed on theoretical grounds by Laurent⁴ and Gerhardt,⁵ and the formula $PNCl_2$, suggested. At a later date, Gladstone and Holmes⁶ revised the work of the former, and adopted Laurent and Gerhardt's formula, at the same time showing, on the basis of the vapor-density, that it must be tripled: $P_3N_2Cl_6$.

Later, Wichelhaus⁷ confirmed the results of Gladstone and Holmes, and suggested the structural formula



and A. W. Hofmann⁸ and Couldridge⁹ added some further observations.

By distilling under diminished pressure the reaction-product of phosphorus pentachloride and ammonia-gas, Besson¹⁰ obtained a substance of the composition $PNCl_2$, which he de-

¹ The part of Wöhler in this investigation seems to have consisted merely in making the analyses for Liebig.

² Q. J. Chem. Soc., **2**, 121, (1850).

³ *Ibid.*, **3**, 135, 353; Ann. Chem. (Liebig), **76**, 74; **77**, 314.

⁴ Compt. rend., **31**, 356, (1850), and Compt. rend. des Trav. de Chimie, (1850), 387.

⁵ Compt. rend. des Trav. de Chimie, (1851), 30; Ann. chim. phys., [3], **18**, 204, note.

⁶ J. Chem. Soc., [2], **2**, 225, (1864).

⁷ Ber. d. chem. Ges., **3**, 163, (1870).

⁸ *Ibid.*, **17**, 1910, (1884).

⁹ J. Chem. Soc., **53**, 398, (1888).

¹⁰ Compt. rend., **114**, 1264, 1480, (1892).

scribes as "un corps solide donnent par sublimation des cristaux très réfringents fusibles à 106° ." The low melting-point would indicate a body other than $P_3N_3Cl_6$ (melting-point 114°), but as the latter is the chief volatile product formed under ordinary circumstances, it may be regarded as an open question whether Besson's compound is identical with Liebig's.

Finally, White¹ and Gilpin² observed it as a secondary product of the action of phosphorus pentachloride on acid ammonium orthosulphobenzoate—doubtless originating in the action of the ammonia.

None of these investigations have thrown much light on the constitution of the chlorophosphuret, or on its relation to other phosphorus compounds.

My attention being called to this substance while engaged in studying the amides of phosphoric acid, I have prepared it in large quantity with a view to further investigation. Although the experiments have not progressed far enough to establish any definite constitutional formula, they show that the chlorophosphuret is by no means as intractable as has been supposed, and that it is one of an homologous series of compounds, having the general formula $(PNC l_2)_x$, which are the chlorides of an homologous series of acids, $(PNO_2H_2)_x$, the *metaphosphimic acids*. From the reaction-product of phosphorus pentachloride and ammonium chloride I have thus far isolated the body $(PNC l_2)_4$, which almost equals $(PNC l_2)_3$ in stability, and which yields, on saponification, an acid $(PNO_2H_2)_4$, also an extremely stable substance. A further product of the reaction is a stable, oily chloride $(PNC l_2)_x$ of high, but as yet unknown, molecular weight. I have also obtained from Liebig's chlorophosphuret the corresponding acid $(PNO_2H_2)_3$, an intermediate chlorhydrine $P_3N_3Cl_4O_2H_2$, and a chloramide $P_3N_3Cl_4(NH_2)_2$. The object of the present paper is mainly to describe the preparation and properties of the chlorides, the consideration of the acids being deferred to a later occasion.

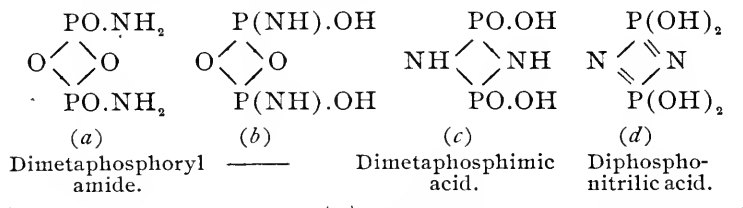
Nomenclature.—In view of the large number of phosphorus-nitrogen compounds actually known or theoretically possible, it is desirable to have a more definite nomenclature than has thus far been used. I have proposed³ to reserve the name

¹ Dissertation, Baltimore: 1891, p. 13. ² Dissertation, Baltimore: 1892, pp. 7, 16.

³ This Journal, 16, 124, note.

amido-orthophosphoric acid for the ortho-acid, in which one hydroxyl is replaced by the amido group, and to call the isomeric form, $P(NH)(OH)_3$, *orthophosphimic acid*. By analogy an acid $P(NH) \begin{smallmatrix} \text{O} \\ \text{---} \\ \text{OH} \end{smallmatrix}$ might be named *metaphosphimic acid*.

Corresponding to the polymeric metaphosphoric acids, we may imagine an homologous series of metaphosphimic acids, but for each of these, several forms would be possible, according as the polymerization is effected by means of oxygen or of nitrogen atoms, assuming them to be otherwise built on the same general type. For example, an acid of the formula $P_2N_2O_4H_4$, with cyclic structure, might have any of the following constitutional formulas, omitting mixed forms:



(a) and (b) represent the amide of a dimetaphosphoric acid with its desmotropic form; (c) and (d) represent the two forms of an acid isomeric with the former, but not directly derivable from a dimetaphosphoric acid. In the former class, phosphorus is united by means of oxygen; in the latter, by nitrogen. (b) and (c) are polymers of $(PO)(NH)(OH)$ while (d) is a polymer of an acid $N \equiv P(OH)_2$, which we may call *phosphonitrilic acid*. Acids of the type (c) I call *x-metaphosphimic acids*, and those of the type (d), *x-phosphonitrilic acids*.¹

In the chlorides $P_3N_3Cl_6$ and $P_4N_4Cl_8$, phosphorus must be united by means of nitrogen² (in the absence of oxygen); hence also in all probability in the acids derived from them. The direct replacement of chlorine by hydroxyl would result in phosphonitrilic acids, but as the type (c) is equally plausible, in the absence of definite experimental grounds, I call them provisionally, *metaphosphimic acids*. For the chlorides

¹ x = mono-, di-, tri-, etc.

² Unless we assume P to be joined to P, and N to N, a view which is not supported by their general behavior.

themselves, instead of the old term chlorophosphuret of nitrogen, which is no longer characteristic, the more definite names *tri-* and *tetraphosphonitrilic chloride* may be used.

EXPERIMENTAL PART.

Preparation of the Chlorides.—The theoretical yield of triphosphonitrilic chloride is 55.5 per cent. of the phosphorus pentachloride; in reality, it falls far below this, no matter what process may be employed, and at best is but a by-product. Gladstone¹ states the yield as about 6 per cent. of the pentachloride (11 per cent. of the theoretical), when 1 molecular weight is distilled with 8 molecular weights ammonium chloride. Couldridge² obtained, by a similar method, a maximum yield of 10 per cent. of the pentachloride (18 per cent. of the theoretical). As a large excess of ammonium chloride is used, much "phospham" is formed. A modification by Gladstone and Holmes,³ consisting in acting on the pentachloride with mercuric chloramide, gave no better results.

I made numerous experiments in sealed tubes, at 200–260°, using sal-ammoniac and pentachloride in theoretical proportions. In this case there is no formation of phospham, but the yield of the desired body is not increased—in fact, seems to be even less than by distilling with an excess of ammonium chloride from an open retort. What results, is a mixture of chloronitrides, largely crystalline, but of very various degrees of solubility and stability towards water, of which but a very small portion is volatile with steam. A study of this mixture would, in all probability, lead to the discovery of other members of the series $(\text{PNCl}_2)_x$.

I finally adopted a slight modification of Gladstone's original method: A mixture (which need not be very intimate) of 1 part pentachloride and 2 parts dry ammonium chloride is rapidly heated in a tubulated retort (one-third filled) fitted to a receiver containing water, which is connected with one or two Woulff's bottles, with water, to condense the small portions carried over with the escaping hydrochloric acid. The water in the receiver should be gently agitated occasionally, in order to break up the crust forming on the surface. When

¹ Q. J. Chem. Soc., **3**, 135; Ann. Chem. (Liebig), **76**, 76.

² J. Chem. Soc., **53**, 399.

³ *Ibid.*, [2], **2**, 227.

the decomposition is about half finished, the heating is interrupted and the hard cake of phospham and sal-ammoniac turned over with a rod inserted through the tubulure; this is necessary as it is so poor a conductor that the bottom of the retort melts before the upper portions of the cake are affected. Heating must not be continued too long, because the subliming ammonium chloride acts on the chlorides condensed in the neck of the retort. After cooling, the substances condensed in the neck are removed by scraping and injecting hot water through the tubulure. The yield varies considerably, according to the quantity of mixture taken; the less the amount, the greater the yield. I have obtained as high as 11.5 per cent. Practically it is not desirable to push this too far, and I have obtained the most satisfactory results by distilling 200 grams of mixture at a time. The proportion of ammonium chloride should not be less than 2 parts, otherwise much pentachloride sublimes unchanged. The distillate, after washing with water, is by no means pure triphosphonitrilic chloride; it is a mixture of chlorides, of which about one-half is quite stable towards cold water, but decomposed on distilling with steam. During this operation, nearly all the triphosphonitrilic chloride, $P_3N_3Cl_6$, is deposited as a hard crust in the condenser. Distillation is continued only as long as much substance passes over; during the later stages, large needles—mainly the new chloride, $P_4N_4Cl_8$ —slowly collect in the condenser. There remain in the flask, besides a strongly acid liquid, a little solid material, consisting partly of phospham, partly of the crystalline acid ammonium tetrametaphosphimate, $P_4N_4O_8H_6(NH_4)_2$, and a considerable amount of oil which solidifies, on cooling, to a crystalline cake of the compound $P_4N_4Cl_8$, impregnated with an oil of the same empirical composition.

The distillate, consisting of triphosphonitrilic chloride, mixed with about 5 per cent. of tetraphosphonitrilic chloride, is dried, and an approximate separation effected by systematic recrystallization from benzene. This solvent has proved the most satisfactory, because the chlorides, in benzene solution, are scarcely affected by water, and no care need be taken to exclude it completely; aqueous ether, on the contrary, acts with considerable ease. The triphosphonitrilic chloride is pure after three or four recrystallizations, the tetraphosphonitrilic

chloride accumulating in the mother-liquors, the residues from which are again subjected to distillation with steam, the substance remaining in the flask being added to the first residue.

Apart from its influence on the melting-point, the presence of very small quantities of the new body in the triphosphonitrilic chloride is readily detected by dissolving in alcohol-free ether and agitating for several hours with a little water, the tetraphosphonitrilic chloride, being indicated by the formation, in the water, of microscopic needles of the difficultly soluble tetrametaphosphimic acid.

The residue from the distillation with steam is sucked out, whereby most of the oily chloride runs through with the water and may be collected. The substance is then dried, the tetraphosphonitrilic chloride, extracted with benzene and purified by several recrystallizations from this solvent. The residue left by the benzene, treated with dilute ammonia, leaves amorphous substances, and gives up tetrametaphosphimic acid, which is thrown down, on acidifying, as its acid ammonium salt. It may be mentioned here that the affinity of this acid for ammonia is such that its acid salt remains undecomposed even in large excess of hot 10 per cent. nitric acid.

The yield of pure chlorides (from 9 kgms. of phosphorus pentachloride) was $P_3N_3Cl_6$, 6.9 per cent. of the pentachloride, $P_4N_4Cl_8$, 0.76 per cent. of the pentachloride, of which 0.42 per cent. was obtained from the residue and 0.34 per cent. from the crude steam-distillate; these are respectively 12.4 and 1.4 per cent. of the theoretical. A further small amount of tetraphosphonitrilic chloride was decomposed during distillation and, in part, recovered as tetrametaphosphimic acid. The yield of oily chloride was not determined, but it was approximately 1 per cent. of the pentachloride.

It is not easy to give a reason for the relatively much higher yield of the triple phosphonitrilic chloride. Doubtless, more of the quadruple compound is formed than is actually obtained, which, because of its less volatility, fails to distill over before it is attacked by the ammonium chloride, and I have also mentioned the simultaneous formation of large quantities of chlorides, unacted on by cold, but decomposed by boiling water. Still, it seems that there is some cause leading to the

predominant formation and greater stability of this body, perhaps analogous to that acting in the case of the aromatic hydrocarbons. The proof that $P_3N_3Cl_6$ is a cyclic compound has not been found, but the occurrence of the number 6 in each case (C_6 and P_3N_3) is possibly more than a mere coincidence. Tetraphosphonitrilic chloride is also possessed of great stability, but I have observed, in various connections, that its chlorine is less firmly held than in the triple compound. The reverse appears to be true of the derived acids, $P_4N_4O_8H_8$ being more stable than $P_3N_3O_6H_6$.

Analytical Methods.—The analysis of these bodies presents no difficulty. The chlorides, which volatilize on heating, are gently warmed with dilute alcoholic soda or potash. In this solution, chlorine is directly determined as silver chloride; phosphorus is determined after evaporating off the alcohol, either by fusing the residue with sodium carbonate or by boiling for one or two hours with strong sulphuric acid, either of which converts it wholly into phosphoric acid. Nitrogen is determined as ammonia after acidifying the saponification product with hydrochloric acid, evaporating the alcohol and boiling the residue with strong sulphuric acid. Experiment showed that no ammonia is evolved during saponification. In the case of the acids and other non-volatile derivatives, the alcoholic saponification is omitted and the substance decomposed either by boiling with concentrated sulphuric acid, or fusing with sodium carbonate, the precaution being taken in the latter case first to moisten the mixture in the crucible. Owing to the strong reducing action of the imido group at high temperatures, these substances cannot be fused alone in platinum without risk to the crucible. This is true even of the salts, which should give pyro- or metaphosphates, on ignition.

The Chlorides.—As *triposphonitrilic chloride* has been the object of previous investigation, and as I have begun several lines of investigation with the object of explaining its nature and relations, I state here only a few incidental observations.

This chloride, as was early observed, has great crystallizing power. The rhombic crystals have been measured by Miller¹ and by Groth.² When pure it tends to form large thick prisms. I have obtained these (from benzene) as much as 8

¹ J. Chem. Soc., [2], 2, 227.

² Ber. d. chem. Ges., 3, 166.

cm. long and 2 cm. wide, their further growth being hindered only by the size of the flask. When impure, it tends to form rhombic or six-sided plates. It fuses at 114° (corr.), while the quadruple chloride, $P_4N_4Cl_8$, fuses at 123.5° (corr.), but a mixture of equal parts is liquid below 90° . The corrected boiling-point is 256.5° at 760 mm. pressure. Besides the solvents elsewhere mentioned (for some of which quantitative data are given below), warm glacial acetic acid dissolves it readily. On boiling this solution with zinc dust, some phosphuretted hydrogen is evolved. Hot concentrated sulphuric acid dissolves it easily. On boiling, some is decomposed, but the greater part distills off unaltered. The rather pleasant aromatic odor of its vapor has long been known. Although this is by no means irritating, inhaling it in any considerable amount is likely to be followed in two or three hours by alarming difficulty in breathing, succeeded by persistent irritation of the air passages. This insidious property renders care necessary in working with it in large quantities or for extended periods, all the more, as the nose is the best instrument for detecting it.

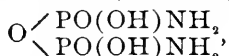
A vapor-density determination by Victor Meyer's method at 360° in dry hydrogen gave 12.35 (calculated 12.01). The volatilization is complete, but on long boiling in air a little solid substance is deposited. Ethyl bromide and sodium are without action on the ethereal solution. Brombenzene and sodium act slowly on the ether or benzene solution, forming a mixture of brownish amorphous organic substances, in part soluble, in part insoluble in ether, in which only a portion of the chlorine is replaced. No smooth reaction could be obtained.

Zinc ethyl, as observed by Couldridge,¹ is without action at ordinary temperature. On heating together in a sealed tube a violent reaction occurs, accompanied by liberation of gas and carbonization. If the zinc ethyl be diluted with 2 vols. benzene, a mixture of complex addition-products is formed on heating, which are left on evaporating as a no longer soluble white vitreous mass, containing zinc, phosphorus, nitrogen, chlorine, and ethyl. This is decomposed by caustic potash, which liberates a mixture of oily bases of a disagreeable sweetish odor, which are for the greater part decomposed on distil-

¹ J. Chem. Soc., 53, 398.

lation, and which dissolve in cold water, and are thrown out on warming. These are slowly decomposed, on heating, with hydrochloric acid into ammonia and what appear to be highly complex phosphinic acids, containing nitrogen. At 170° considerable quantities of combustible gases, and of mono-, di-, and triethyl phosphine are formed by the action of zinc ethyl, in addition to a small amount of a crystalline basic substance containing nitrogen, and showing much the same properties as the oily substances alluded to. The yield was very minute.

Action of Water on Triphosphonitrilic Chloride.—By decomposing chlorophosphuret of nitrogen with aqueous ether,¹ or with alcoholic alkalies,² Gladstone obtained a substance which he named deutazophosphoric acid. He afterwards obtained this in larger quantity by treating phosphorus oxychloride with dry ammonia, and assigned to it the formula



and the name pyrophosphodiamic acid. The formation of such an acid can only be due to a deep decomposition of the molecule.

Although unacted on by water alone or by anhydrous ether alone, I have found that a smooth decomposition is easily effected by dissolving the chlorophosphuret in alcohol-free ether, and shaking this solution a long time with water, whereby intimate contact is effected. The final products are hydrochloric acid and an acid in which the chlorine is wholly replaced by oxygen and hydrogen, without further change. I have named this substance, $\text{P}_3\text{N}_3\text{O}_6\text{H}_6$, *trimetaphosphimic acid*.³ If the water contain bases or acetates in solution, the salts are directly obtained. As the acid will be described in a separate paper, I mention here only that it is extremely soluble and totally devoid of crystallizing power, but forms some

¹ Q. J. Chem. Soc., **3**, 135, 354; Ann. Chem. (Liebig), **76**, 79; **77**, 315.

² J. Chem. Soc., [2], **2**, 231.

³ According to Mente, (Ann. Chem. (Liebig), **248**, 241, 244), Gladstone's pyrophosphodiamic acid is really $\text{NH} \begin{array}{c} \diagup \text{PO} \\ \diagdown \text{PO} \end{array} \text{NH}$, *i. e.*, dimetaphosphimic acid, which has the

same empirical composition as trimetaphosphimic acid. Mente did not obtain his acid from triphosphonitrilic chloride, but from phosphorus oxychloride, and it is not clear that it is really identical with Gladstone's acid from chlorophosphuret of nitrogen. The independent existence and stability of the tetra-acid affords a presumption that other members of the series can exist also.

salts of characteristic crystalline form, and has a strong tendency to form double salts, one of these, $P_3N_3O_6H_3NaBa$, giving especially fine crystals.

As intermediate products, chlorhydrines have been observed. Theoretically, five of these are possible, one of which I have isolated; namely,

Triphosphonitrilic-tetrachlorhydrine, $P_3N_3Cl_4O_2H_2$. — 1 part triphosphonitrilic chloride is dissolved in 10 parts alcohol-free ether, and the solution agitated with about one-third its volume of water for six to eight hours, best by means of a small turbine. The water then contains hydrochloric acid and trimetaphosphimic acid, and the ether contains the chlorhydrines and unchanged chloride. The ether is dried over calcium chloride, and the greater part distilled off in the water-bath, the latter portions being removed at ordinary temperature by a current of dry air. The residue consists of unchanged chloride, the chlorhydrine in question, and small quantities of others. The greater part of the chloride is removed by a little benzene, and the residual chlorhydrine well washed with carbon disulphide. The yield depends somewhat on the time the water has acted, but as there is a continuous conversion of chloride into chlorhydrine, and of the latter into trimetaphosphimic acid, the amount present at any one time is not great. Under the above conditions it was about 10 per cent. of the theoretical, fully one-half the chloride being recovered.

Analysis gave:

	Calculated for $P_3N_3Cl_4O_2H_2$.	(1)	Found. (2)	(3)
P.....	29.94	30.00	30.04
N.....	13.54	13.74
Cl.....	45.59	45.38	48.18	48.37

Ratios: (2) P : N : Cl = 3 : 3.03 : 4.20.

(3) P : Cl = 3 : 4.23.

(1), (2), and (3) represent different preparations, (1) having been further purified by recrystallizing from benzene.

The chlorhydrine forms a white sandy powder, consisting of well-defined, microscopic prisms. It is very difficultly soluble in boiling benzene, and is insoluble in benzene and in carbon disulphide. With the latter it shows a peculiar behavior.

Its refractive index is such that it nearly vanishes and apparently dissolves when brought into the disulphide ; on decanting the liquid the moist powder shows beautiful iridescence. Alcohol dissolves it easily and in ether it is much more soluble than the original chloride, the presence of a trace of ether vapor causing it to liquefy instantly. Water dissolves it somewhat slowly, but abundantly, the solution containing hydrochloric acid and trimetaphosphimic acid, the latter being left on rapid evaporation on the water-bath or *in vacuo*, as a transparent, easily soluble gummy residue. From the aqueous solution of the chlorhydrine, salts of trimetaphosphimic acid were directly prepared and analyzed. The chlorhydrine is quite stable in the air at ordinary temperature,¹ but on heating at 100° it slowly increases in weight through absorption of moisture, undergoing decomposition with formation of ammonium chloride. It shows no definite melting-point, but, on rapid heating, liquefies imperfectly, gives off hydrochloric acid, and leaves a mixture of amorphous substances of different degrees of solubility in water.

Other chlorhydrines, partly crystalline, appear to be formed simultaneously, but in relatively small amount, and their isolation is attended with difficulties. Whether the two chlorine atoms removed are associated with the same or with different phosphorus atoms remains to be determined.

Triphosphonitrilic Chloramide, $P_3N_3Cl_4(NH_2)_2$.—The tendency to the formation of stable bodies in which one-third of the chlorine is substituted, observed in the case of the chlorhydrine appears if triphosphonitrilic chloride be acted on in ether solution by ammonia. Gaseous ammonia may be used, but this is by no means necessary, aqueous ammonia producing the same result. If the chloride be dissolved in ether and shaken a short time with 10 per cent. ammonia, but one amide appears to be formed. As soon as a few drops of the ether solution leave, on evaporation, a residue completely soluble in hot water, indicating complete transformation of the chloride, it is dried over calcium chloride and allowed to evaporate spontaneously, whereby a substance crystallizing in needles is deposited. The product, which appeared homogeneous on microscopic examination, was directly analyzed.

¹ On keeping for several months, a slight formation of ammonium salts was observed.

	Calculated for $P_3N_3Cl_4(NH_2)_2$.	Found.
P.....	30.12	29.51
N.....	22.72	21.98
Cl.....	45.86	44.83

Ratio: $P:N:Cl = 3:4.94:3.98$.

The yield was 67 per cent. of the theoretical, some of the chloride having been further decomposed and dissolved by the ammonia.

Triphosphonitrilic chloramide is quite soluble in ether, and less soluble in hot benzene, from which it crystallizes in long tufts of delicate hairs. It is easily soluble in alcohol, and from the concentrated alcoholic solution it is precipitated by water. Its stability towards water is striking; cold water dissolves it slightly, and, on rapid evaporation, even on the water-bath, much is deposited unaltered; it can even be recrystallized from hot water, though with much decomposition, in needles or short prisms. Its stability in aqueous solution is further indicated by the failure of silver nitrate to give a precipitate except on boiling. Aqueous ammonia has but little action in the cold. On heating its aqueous solution, ammonium chloride and a syrupy acid result. Cold dilute acids have no marked solvent action. It gradually undergoes change at ordinary temperature, and rapidly on heating, without fusing, ammonium chloride and an infusible white substance being the products in the latter case.

Couldridge,¹ by acting on fused triphosphonitrilic chloride with gaseous ammonia, obtained a substance which he regarded as phospham. Both Couldridge and A. W. Hofmann² express the opinion that phospham has the composition expressed by the formula $P_3N_3(NH)_3$. I regard this as too sweeping. Apart from the fact that its composition varies with the mode of preparation,³ it is likely that the true phospham is a mixture of an homologous series of imides $(PN.NH)_x$, derivable from the homologous phosphonitrilic chlorides, $(PNCl_2)_x$.

Tetraphosphonitrilic Chloride, $P_4N_4Cl_6$.—The new chlorophosphuret of nitrogen, prepared as above described, gave the following results on analysis:

¹J. Chem. Soc., 53, 398.

²Ber. d. chem. Ges., 17, 1911.

³Salzmann: Ber. d. chem. Ges., 7, 494.

	Calculated for $P_4N_4Cl_8$.	Found.	
		(1)	(2)
P.....	26.77	26.89	27.00
N.....	12.11	12.35	12.36
Cl.....	61.12	61.17	61.28
Ratios :	(1) P : N : Cl = 1 : 1.01 : 1.99.		
	(2) P : N : Cl = 1 : 1.01 : 1.99.		

(1) and (2) represent different preparations.

The vapor-density, determined by Victor Meyer's method, in dry hydrogen at 360° , was :

	Calculated for $P_4N_4Cl_8$.	Found.
Density.....	16.03	16.20

I am indebted to Mr. B. H. Hite, of the Johns Hopkins University, for a series of determinations of the molecular weight by the ebullioscopic method. The following is his statement of the results :

Solvent : Benzene. Molecular elevation 26.7 .

Substance $(PNCl_2)_x$.

Grams solvent.	Grams substance.	Concentration.	Elevation.	Molecular weight found.	Percentage variation from 464.
37.618	1.1620	3.09	0.177°	466	+0.4
37.618	1.4820	3.94	0.227°	463	-0.2
37.987	1.1107	2.92	0.167°	467	+0.7

These results agree well with the quadruple formula.

The following table gives some of the constants compared with those of $P_3N_3Cl_6$.

	$P_3N_3Cl_6$.	$P_4N_4Cl_8$.
Specific gravity.....	1.98 ¹	2.18 ²
Melting-point (Corr.).....	114°	123.5°
Boiling-point, (760 mm. pressure ; thermometer wholly in vapor)..<	256.5°	328.5°
100 parts ether at 20° dissolve....	46.5	12.3
100 parts benzene at 20° dissolve.	57.4	20.9

Tetraphosphonitrilic chloride forms colorless, brittle prisms, not easily wet by water, and therefore having a strong tendency to float. Superficially, these are not always to be distinguished from those of triphosphonitrilic chloride, but in a general way it may be said that they tend to be much smaller, and are to be measured by millimeters rather than centimeters, and that they tend to vary towards an acicular, rather

than a tabular form. In alcohol and in benzine it is much less soluble than $P_3N_3Cl_6$. Hot concentrated sulphuric acid dissolves it, and, on boiling, much hydrochloric acid is evolved, but some of the substance sublimes out unchanged. It may be recrystallized from glacial acetic acid; on boiling this solution with zinc dust, a little hydrogen phosphide is given off, and the solution contains ammonia.

It is perceptibly volatile at its fusing-point, its vapor having an odor suggesting, but perceptibly differing from that of triphosponitrilic chloride and less aromatic. The fused substance solidifies to a mass of nearly parallel needles, while triphosponitrilic chloride gives transparent plates. As mentioned above, its volatility with steam is comparatively slight. If boiled for some time in contact with air a minute amount of substance is formed which swells enormously to a clear gelatinous mass in benzene. Alcohol converts it slowly into an oily ether, which aqueous ammonia, on warming, saponifies to tetrametaphosphimic acid.

Action of Water on Tetraphosponitrilic Chloride.—In its chemical behavior it resembles triphosponitrilic chloride. It is scarcely acted on by boiling water, yet on prolonged boiling, a minute amount of tetrametaphosphimic acid is formed; aqueous fixed alkalies are without perceptible action, while alcoholic alkalies decompose it easily, but the product is mainly something else than tetrametaphosphimic acid.

A smooth decomposition is effected by dissolving in ether and shaking protractedly with water. The first products of this action consist of chlorhydrines, which remain dissolved in the ether, are crystalline, and readily soluble in cold water, from which solution tetrametaphosphimic acid is rapidly deposited in the form of thick needles; the same acid is the final product of the action of water on the ether solution.

The action of water proceeds rather more rapidly than in case of triphosponitrilic chloride, but many days are required for complete decomposition. The small amount of material, at present in my possession, made it unadvisable to attempt to isolate any of the chlorhydrines, of which seven are theoretically possible

Tetrametaphosphimic Acid, $P_4N_4O_8H_8 + 2H_2O$, will be described in a separate paper. It may be remarked here pre-

liminarily that it has highly characteristic properties, is highly crystalline, very difficultly soluble in cold water, and much less soluble in dilute acids, that it readily decomposes soluble chlorides, nitrates, and sulphates, and gives three series of salts, in which respectively one-fourth, one-half, and all the hydrogen is replaced by metal; many of these show characteristic forms. The free acid far surpasses the metaphosphoric acids in stability and may be boiled for hours with nitric acid or *aqua regia* without much decomposition.

Tetraphosphonitrilic chloride is readily extracted from its ethereal solution by aqueous ammonia, the ammoniacal solution giving tetrametaphosphimic acid on warming with hydrochloric acid. No clear evidence of the formation of chloramides has yet been observed.

Oily Phosphonitrilic Chloride.—This substance, obtained from the residues as above stated, has not yet been carefully studied; it is possibly a mixture. It is scarcely volatile without decomposition, not volatile with steam, and not acted on by water, except in ethereal solution, when a moderately soluble phosphimic acid is slowly formed, which crystallizes in needles, and decomposes on warming with water into tetrametaphosphimic acid and ammonium phosphate. The analysis gave:

	Calculated for (PNC _l) _x .	Found.
P.....	26.77	26.73
N.....	12.11	12.09
Cl.....	61.12	61.89

Ratio : P : N : Cl = 1 : 1 : 2.03.

U. S. GEOLOGICAL SURVEY, WASHINGTON,
February, 1895.

ON THE SAPONIFICATION OF THE ETHERS OF THE SULPHONIC ACIDS BY ALCOHOLS.

BY J. H. KASTLE AND PAUL MURRILL.

Many observers have doubtless been impressed with the peculiar differences existing between the carbonic and the sulphonic acids. Some of these differences which have been observed to exist, to some of which we believe that attention is here called for the first time, are as follows:

(1) The great difference in the strength of these two classes

of acids—the sulphonic acids being remarkably strong—the carbonic acids weak.

(2) A striking difference in the stability of their acid chlorides. Many of the acid sulphon-chlorides may be boiled with water for some little time without risk of decomposition, whereas the acid chlorides of the carbonic acids decompose with remarkable ease by such treatment.

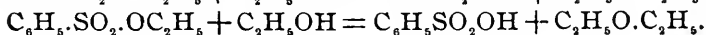
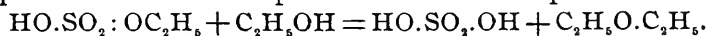
(3) A difference is observed in the conduct of the amides of these two classes of acids towards water and dilute acids—the sulphonic amides undergoing no decomposition when boiled with a dilute acid, while in this manner the amides of the carbonic acids are readily changed into their acid and an ammonium salt.

(4) Another very striking difference is to be found in the stability and conduct of the ethereal salts of these two kinds of acids towards water and alcohol—the ethereal salts of the carbonic acids being stable and saponifying with difficulty, whereas the ethereal salts of the sulphonic acids are unstable—decomposing largely upon boiling—and are readily saponified in several ways. For example, it has been observed by one of us—Kastle¹—that, by boiling the diethyl ether of a sulphon-carbonic acid, *viz.*, diethyl-(*p*)-nitrosulphobenzoate,

$$\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{COOC}_2\text{H}_5 \\ \text{SO}_2\text{OC}_2\text{H}_5 \\ \diagdown \text{NO}_2 \end{array}$$
, with water or with alcohol, the ethyl sulphonate part of the compound very easily underwent saponi-

fication, yielding an acid,
$$\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{COOC}_2\text{H}_5 \\ \text{SO}_2\text{OH} \\ \diagdown \text{NO}_2 \end{array}$$
, whereas the ethyl carbonate group underwent no alteration.

Since the time of these observations Krafft and Ross² have made a study of the methods of preparation of the sulphonic ethers and of their peculiar conduct towards alcohol. These observers have pointed out that ethers (alkyl oxides) are formed as the result of the action of a sulphonic ether and alcohol, and have called attention to the similarity between sulphuric acid and the sulphonic acids in this respect.



¹ This Journal, **11**, 177.

² Ber. d. chem. Ges., **25**, 2255; and **26**, 2823, and 2829.

They have also shown that this reaction might be taken advantage of in the preparation of ethers, (alkyl oxides) simple and mixed. In fact by the action of alcohols upon the sulphonic ethers at somewhat elevated temperatures they succeeded in preparing several ethers which, hitherto, by the usual methods, had only been prepared with difficulty and in small quantities. In order to compare accurately the conduct of the carbonic and sulphonic acids in regard to the reaction of their ethereal salts towards absolute alcohol, small weighed quantities of ethyl benzoate and ethyl benzenesulphonate were heated in sealed tubes in boiling water for one-half hour with 50 times the required quantity of absolute ethyl alcohol. In this time 45 per cent. of the ethyl benzenesulphonate were saponified while of the ethyl benzoate only 3 per cent. were saponified. It was with the view of making a thorough study of the kinetics of the saponification of the sulphonic ethers by means of alcohol that this investigation was undertaken. The first preliminary experiments were made by Mr. H. H. Hill, with results not altogether satisfactory, owing to impure material. A careful study of the methods employed in making the sulphonic ethers has put into our hands a better material. Nevertheless our studies along this line are by no means complete. The results, however, are believed to be accurate and of sufficient interest to warrant this preliminary notice.

The following ethereal salts were selected for the investigation: Ethyl benzenesulphonate, ethyl (*p*)-chlorbenzenesulphonate, ethyl (*p*)-brombenzenesulphonate, and ethyl (*p*)-iodobenzenesulphonate. Of these the first three are known and require no word of description. Perhaps a word regarding the last one of which no mention is made in the literature may not be out of place in this connection.

Ethyl (p)-Iodobenzenesulphonate.—This compound was prepared by treating (*p*)-iodobenzenesulphonchloride dissolved in absolute ether with sodium ethylate. By recrystallization from ether it was obtained in fine, four-sided, transparent prisms, which were found to melt at 51° C. (uncor.). It was without odor, insoluble in cold water, slightly soluble in hot, and very easily soluble in alcohols and ether.

Action of Different Alcohols upon Sulphonic Ethers at Ordinary Temperature.

The first experiments along this line were tried with ethyl benzenesulphonate and several alcohols, each in various proportions, for thirty days at ordinary temperature. Small quantities of the ether, about 0.25 gram, were placed in a tightly-stoppered flask with 1, 10, 50, 100, 500, and 1,000 times the quantity of the alcohol required for its saponification. These experiments were concluded at the end of thirty days, and the extent of the saponification determined by titration with $\frac{1}{10}$ N. caustic potash. In the following table, No. 1, are to be found the results of these experiments :

TABLE I.
Proportion of alcohol to ether.

Kind of alcohol.	1:1	10:1	50:1	100:1	500:1	1000:1			
Methyl...	1.61	20.38	26.85	25.65	23.03	23.04	per cent.	saponification.	
Ethyl	2.04	17.52	19.20	18.47	17.31	16.30	"	"	"
N-Propyl.	3.81	15.55	16.94	17.65	17.36	"	"	"
Iso-propyl	1.86	13.45	19.36	20.30	19.72	19.88	"	"	"

These results show first that the saponification takes place readily even at ordinary temperatures ; and secondly, that the rate of saponification is very nearly the same for all of the alcohols employed except for methyl alcohol, for which it is decidedly greater ; and, thirdly, that the maximum of saponification is reached with from 50 to 100 times the required quantity of the several alcohols employed. The fact that larger quantities than these cause a falling off in the amount of saponification in a given time would seem to indicate that with very large quantities of alcohol the saponification would be altogether checked, for the reason probably that by mass action the large quantities of alcohol would tend to reform the ethers as rapidly as it was saponified.

Similar results, with two alcohols, were obtained with ethyl (*p*)-brombenzenesulphonate as shown in the following table, No. II :

TABLE II.
Proportion of alcohol to ether.

Kind of alcohol.	1:1	10:1	50:1	100:1	500:1	1000:1			
Methyl...	1.60	42.15	50.38	49.28	45.00	44.73	per cent.	saponification.	
Ethyl	3.24	35.00	40.27	37.86	36.64	38.00?	"	"	"

In this case it is also seen that a maximum of saponifica-

tion is reached with 50 times the required quantity of the alcohol; and also the same difference is observable in the action of the two alcohols, the methyl being decidedly the more active.

In order to compare the rates of saponification of the halogen ethers with that of the ethyl benzenesulphonate, small, weighed quantities of the several ethers were allowed to stand in tightly-stoppered flasks for twenty-two days, at ordinary temperature, with 50 times the required quantity of ethyl and methyl alcohol. The results are to be found in the following table, No. III:

TABLE III.

Kind of alcohol.	Ethyl benzenesulphonate.	Chlor-ether.	Brom-ether.	Iodo-ether.	
Methyl....	13.11	28.26	31.05	28.65	per cent. saponified.
Ethyl....	8.78	21.05	21.34	20.44	" " "

From these results it will be easily seen that the halogens exert a very great influence on the rate of saponification; and that, curiously, each of the halogens increases the rate of saponification to the same extent; and here again it will be observed that in every case the methyl alcohol acts more strongly than the ethyl.

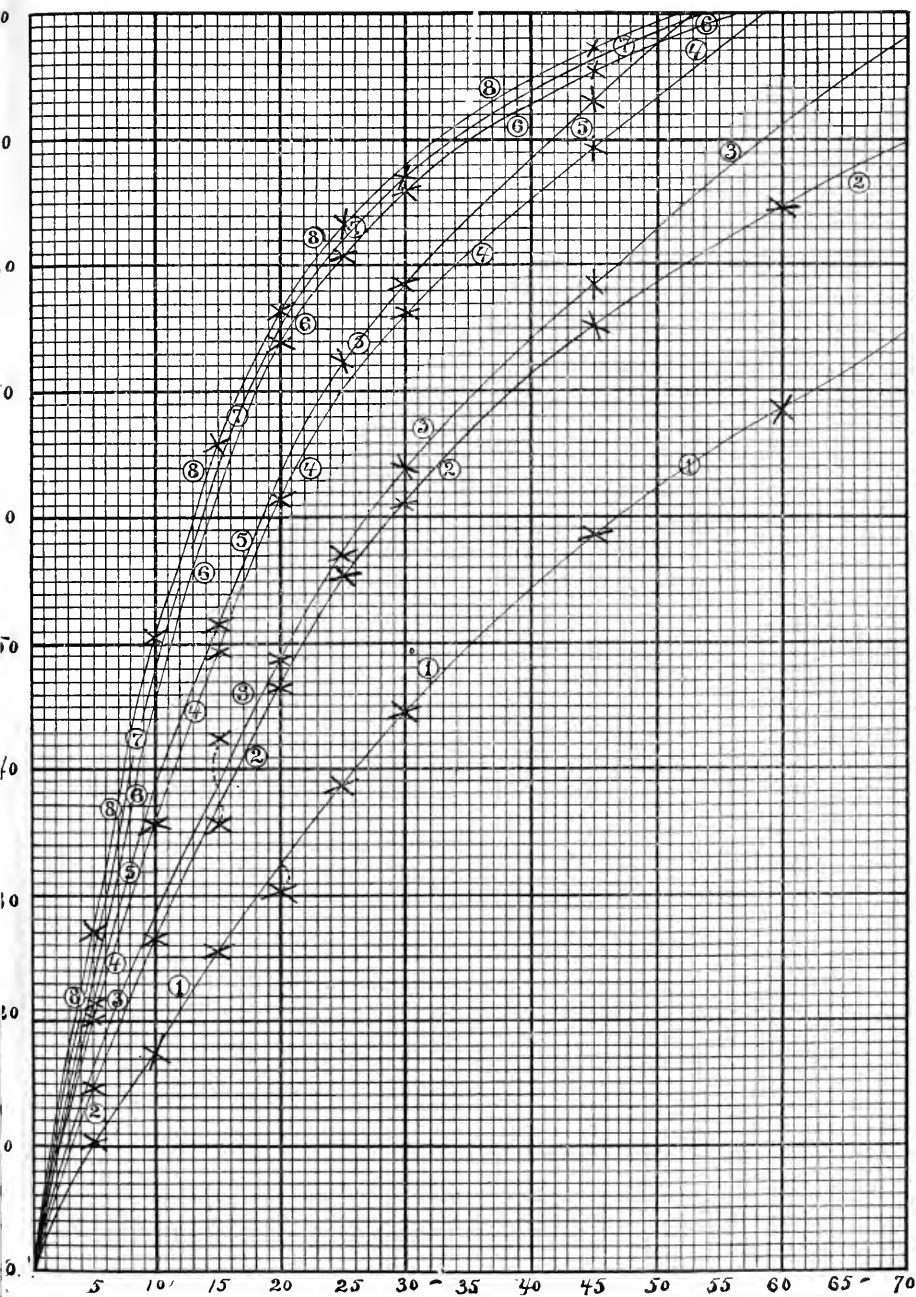
On the Action of Methyl and Ethyl Alcohols upon the Sulphonic Ethers at 100° C.

It was also deemed expedient to try the effect of higher temperatures upon the saponification of these ethers. Accordingly, small, weighed quantities of each of the above-mentioned ethers were heated in small sealed tubes in boiling water with 50 times the required quantity of alcohol. Ethyl and methyl alcohols were used in the experiments. Experiments with each ether were tried for five, ten, fifteen, twenty, twenty-five, thirty, and forty-five minutes, and one hour, except when otherwise indicated in tables Nos. IV, V, VI, and VII, in which are to be found the results of these experiments. These results have also been plotted as curves, (see p. 295) with the several intervals of time for abscissae and the percentages of saponification as ordinates.

TABLE IV.

Ethyl benzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.	1 hour.	
Methyl.	14.13	26.45	35.66?	46.67	55.12	60.87	75.52	84.5	per cent. sapon.
Ethyl ..	9.26	17.59	25.46	30.87?	38.31	44.52	58.43	68.65	" "



1. Ethyl sulphobenzoate with ethyl alcohol.
2. Ethyl sulphobenzoate with methyl alcohol.
3. Chlor-ether with ethyl alcohol.
4. Iodo-ether with ethyl alcohol.

5. Brom-ether with ethyl alcohol.
6. Chlor-ether with methyl alcohol.
7. Brom-ether with methyl alcohol.
8. Iodo-ether with methyl alcohol.

TABLE V.

Ethyl (p)-Chlorbenzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.		
Methyl.	25.06?	57.15?	73.91	81.04	85.82	95.23	per cent.	sapon.
Ethyl ..	23.00?	37.91?	42.68	58.37	66.73	73.09	88.01	"	"

TABLE VI.

Ethyl (p)-Brombenzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.		
Methyl.	27.58	64.95	86.89	100.00?	per cent.	sapon.
Ethyl ..	20.87	51.16	78.3	93.16	"	"

TABLE VII.

Ethyl (p)-Iodobenzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.		
Methyl.	27.13	50.60	65.27	76.46	83.46	96.47?	96.98	per cent.	sapon.
Ethyl ..	20.00	35.54	49.56	61.54	72.10?	76.41	89.63	"	"

The effect of raising the temperature is to greatly increase the saponification; otherwise practically the same relations hold for the reactions that were observed for lower temperatures; that is, the saponifying effect of methyl alcohol is greater than that of ethyl; and the ethers of the halogen benzenesulphonic acids are more easily saponified than that of ethyl benzenesulphonate; and except for the ethyl (*p*)-chlorbenzenesulphonate with ethyl alcohol, each of the halogens seems to accelerate the saponification to the same degree.

A consideration of the curves on p. 295, brings out these points very clearly. The curves for the halogen ethers saponified by methyl alcohol are sufficiently near to each other and so nearly concentric as to be considered identical. The curves representing the saponification of the halogen ethers by ethyl alcohol are also in the case of the iodo and the brom-ether sufficiently near together to be considered the same, whereas the curve for the chlor-ether, diverges somewhat from both of the above. Lastly, the curves representing the saponification of the benzenesulphonic ether with ethyl and methyl alcohol are clearly divergent from those of the halogen ethers and also from each other.

Conclusions.

From the experiments above described the following conclusions may be drawn:

(1) The ethers of the sulphonic acids are easily saponified by alcohols.

(2) A rise of temperature causes a great increase in the rate of saponification.

(3) Of the alcohols tried, methyl alcohol is undoubtedly the most powerful in its action, while the other alcohols seem to be about the same in their action.

(4) The replacement of hydrogen by a halogen in the sulphonic acid renders the ethereal salts of the substituted acid more easy to saponify.

(5) Except in one case, no difference, save such as could be brought within the limits of experimental error, was observable in the rate of saponification of the ethers of the halogen sulphonic acids, thereby indicating these three halogens to be alike in their capacity to accelerate the saponification of a sulphonic ether.

STATE COLLEGE OF KENTUCKY, LEXINGTON,
February, 1895.

Contributions from the Chemical Laboratory of Harvard College.

LXXXVI.—ON THE CUPRIAMMONIUM DOUBLE SALTS.

THIRD PAPER.¹

BY THEODORE WILLIAM RICHARDS AND GEORGE OENSLAGER.

The work already done upon the double salts of cupriammonium² suggested the possibility of obtaining compounds of fluorine and iodine similar to those of chlorine and bromine.

Many attempts were made to prepare cupriammonium aceto-fluoride, $\text{Cu}(\text{NH}_3)_2\text{FC}_2\text{H}_3\text{O}_2$ with invariable failure. The methods and the proportions of the various reagents were varied in every possible way; but nothing could be obtained beside cupriammonium acetate and ammonium fluoride. Cupriammonium fluoride itself is very difficult to prepare, because of its solubility; and it is not strange that the double salt should be more so. It will be remembered, moreover, that while cupriammonium acetobromide is very easily

¹ Presented to the American Academy of Arts and Science, June 9, 1894.

² Richards and Shaw: this Journal, **15**, 642; also Richards and Whitridge: this Journal, **17**, 145.

obtained, the normal acetochloride is made with great difficulty by ordinary crystallization. We should expect the fluorine compound to be even less easily formed. Because of these continued failures, the work with fluorine was discontinued.

The investigation of the compounds of iodine proved much more fruitful, yielding the following new substances:

- (1) $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$;
- (2) $7\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$;
- (3) $\text{Cu}_3(\text{NH}_3)_{10}\text{I}_6$;
- (4) $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\text{NH}_4\text{C}_2\text{H}_3\text{O}_2\cdot\text{H}_2\text{O}$;

besides confirming the work of Foerster¹ on the following substances:

- (5) $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2$.
- (6) $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2\frac{1}{2}\text{H}_2\text{O}$.

(1) AMMON-CUPRIAMMONIUM ACETOIODIDE,
 $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$.

In preliminary experiments the following method was used for preparing this compound: 4 grams of finely powdered cupric acetate were stirred with a mixture of 10 cc. of water, 20 cc. of alcohol, and 8 cc. of glacial acetic acid. Ammonia gas was then passed into the mixture until all the cupric acetate was dissolved and the color of the solution had become a deep blue. After the addition of 3.5 grams of ammonic iodide, the solution was set aside to crystallize and, in about six hours, large deep-blue, monoclinic plates having a six-sided outline, separated out. These crystals were washed with alcohol, and then dried between filter-papers as rapidly as possible. The salt thus prepared is usually not very pure, hence subsequently more alcohol was used in the preparation, with better success. Even yet, however, there was room for improvement.

After many systematic experiments which need not be detailed, the following method was found to yield excellent results: 12 grams of cupric acetate were dissolved in 50 cc. of ammonia-water (sp. gr. = 0.90) in a flask. After cooling, 30 cc. of aqueous acetic acid (57-per cent.) were added to the solution, then 6 grams of ammonic iodide, and finally 50 cc. of alcohol. Upon boiling on the water-bath, the mixture

¹ Ber. d. chem. Ges., 25, 3412.

yielded a clear, deep-blue solution, which deposited crystals of ammon-cupriammonium acetoiodide upon slow evaporation in the air. The first very small crop of crystals deposited upon cooling was not analyzed. The second served for analysis IV below, and the third crop for analyses V and VIII. The substance used in analyses I, II, III, VI, and VII was prepared by earlier, less satisfactory, methods; it was undoubtedly the same substance, however.

Ammon-cupriammonium acetoiodide consists of brilliant, deep-blue, crystalline, monoclinic plates. It is not very permanent in the air, although much more so than its chlorine and bromine analogues. Upon exposure for a long time, the crystals become dull and dark in color, and the substance slowly loses in weight. Water at once decomposes it, some of the copper going into solution, and the rest remaining as a basic precipitate. Acids set iodine free, and precipitate cuprous iodide, as might be expected. The only unexpected property of the salt is the fact that it contains no crystal-water, thus not maintaining a strict analogy with the chlorine and bromine compounds, $\text{Cu}(\text{NH}_3)_3\text{ClC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$. The reason for this anomaly remains obscure.

The ammonia present in the compound was determined by distillation with pure potash or soda, the distillate being titrated with standard acid. It is convenient to prepare the alkali for this purpose directly from metallic sodium or from sodium-amalgam, thus avoiding the complications in the subsequent proceedings introduced by the usual impurity of chlorine in commercial alkali. The residue in the distilling flask, after the ammonia had been expelled, was filtered, and to the filtrate was added a little sulphurous acid to reduce any iodate which might have been formed. Argentic nitrate was then added, and afterwards the argentic oxide and sulphite were dissolved by nitric acid, the argentic iodide being collected and weighed upon a Gooch crucible. In analysis IV the alkali was nearly neutralized, and in analysis V the solution was just acidified by pure nitric acid before the precipitation. In every case enough nitric acid was added after the precipitation to insure the solution of all but argentic iodide, and the agreement of the results is sufficiently satisfactory. The

copper was determined by electrolysis of the cupric sulphate obtained from the precipitated cupric oxide, which contained no trace of iodine¹; and the acetic acid was determined by combustion.

Analyses of $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$.

I. 0.2591 gram of the substance, on distillation with potash, required 25.34 cc. of decinormal acid for neutralization, gave, on electrolysis, 0.0545 gram of copper, and yielded 0.2042 gram of argentic iodide.

II. 0.2524 gram of the substance required 25.05 cc. of decinormal acid, and gave 0.0527 gram of copper.

III. 0.2322 gram of the substance required 23.25 cc. of decinormal acid.

IV. 0.3960 gram of the substance gave 0.3109 gram of argentic iodide.

V. 0.2559 gram of the substance gave 0.2004 gram of argentic iodide.

VI. 0.3211 gram of the substance gave, on combustion, 0.0931 gram of carbon dioxide.

VII. 0.2946 gram of the substance gave, on combustion, 0.0864 gram of carbon dioxide.

VIII. 0.3062 gram of the substance gave, on combustion, 0.0907 gram of carbon dioxide.

No.	Copper.	Ammonia.	Iodine.	Acetic acid.
I.	21.03	16.73	42.58
II.	20.88	16.95
III.	17.10
IV.	42.41
V.	42.31
VI.	19.46
VII.	19.67
VIII.	19.86
Average,	20.96	16.93	42.43	19.66
Calculated for $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$.				Found.
Copper	21.15			20.96
Ammonia.....	17.03			16.93
Iodine.....	42.19			42.43
Acetic acid.....	19.63			19.66
	100.00			99.98

¹ Tested in analyses IV and V.

(2) OCTO-CUPRIAMMONIUM MONOIODIDE ACETATE.

On allowing the mother-liquor remaining from the first method of preparing ammon-cupriammonium acetoiodide to stand for a long time, large coal-black hexagonal crystals of unknown composition were deposited. Mixed with these were large blue crystals, which were separated mechanically from the black ones, and analyzed. The analysis corresponded closely with the formula $7\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Cu}(\text{NH}_3)_2\text{IC}_2\text{H}_3\text{O}_2$, the complexity of which led to the suspicion that the crystals were a mixture instead of a definite compound. Nevertheless, upon testing, the smallest as well as the largest crystals were found to contain iodine. In external appearance the crystals, which were usually at least half a centimeter in length, resembled those of cupriammonium acetate. An attempt was made to measure the angles of the crystals of each substance, but the faces were so covered with striations that the result was only partially satisfactory. For cupriammonium acetate the chief prism angle was about 70° , while for the complicated salt under discussion it was over $71^\circ 30'$. Even allowing a considerable margin for possible error, it would appear that the complicated salt must be a definite compound, and not merely cupriammonium acetate containing occluded cupric acetate and ammonic iodide. Another evidence of the probable definiteness of the salt is to be found in the fact that Richards and Moulton, in a paper yet to be published, have proof of the existence of a similar compound containing aniline and bromine instead of ammonia and iodine. The compound has no unexpected properties, and was analyzed in the usual fashion.

Analyses of $\text{Cu}_8(\text{NH}_3)_{16}\text{I}(\text{C}_2\text{H}_3\text{O}_2)_{16}$.

I. 0.2545 gram of the substance, distilled with soda, required 22.68 cc. of decinormal acid, gave 0.0333 gram of argentic iodide, and, on electrolysis, yielded 0.0707 gram of copper.

II. 0.2120 gram of the substance required 18.52 cc. of decinormal acid.

III. 0.2419 gram of another sample of the substance required 21.23 cc. of acid, and gave 0.0331 gram of argentic iodide and 0.0680 gram of copper.

No.	Copper.	Ammonia.	Iodine.
I.	27.78	15.25	7.07
II.	14.93
III.	28.11	14.99	7.39
	<hr/>	<hr/>	<hr/>
	27.95	15.05	7.23
Calculated for			
$\text{Cu}_3(\text{NH}_3)_{16}\text{I}(\text{C}_2\text{H}_3\text{O}_2)_{15}$.			
Copper	28.35		27.95
Ammonia	15.22		15.05
Iodine	7.07		7.23
Acetic acid (by difference)	49.36		49.77
	<hr/>		<hr/>
	100.00		100.00

Every effort to make the normal cupriammonium acetoiodide, $\text{Cu}(\text{NH}_3)_2\text{IC}_2\text{H}_3\text{O}_2$, free from cupriammonium acetate was unsuccessful; when so much of the ammonia has evaporated that the salt $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$ ceases to form, the singular double salt which has just been described always makes its appearance.

(3) TETRAMMON-TRICUPRIAMMONIUM IODIDE,
 $3\text{Cu}(\text{NH}_3)_2\text{I}_2 + 4\text{NH}_3 = \text{Cu}_3\text{I}_6(\text{NH}_3)_{10}$.

This interesting substance may be prepared by a method very closely resembling that used for preparing ammoncupriammonium acetoiodide. If 8 grams instead of 12 grams of cupric acetate be used with 50 cc. each of ammonia and of alcohol, 30 cc. of acetic acid, and 6 grams of ammonic iodide, curious black crystals resembling irregular triangular pyramids make their appearance in the first place.

The new substance is somewhat similar in aspect to the corresponding bromine compound¹ although less brilliant. The crystalline faces are so singularly marked and striated that an accurate crystallographic study would not be feasible. They possess a distinct bronze lustre which soon disappears, owing to superficial decomposition. Upon exposure to the air the substance loses ammonia and iodine, finally leaving cuprous iodide. It is decomposed by water. Heated in aqueous or alcoholic ammonia it dissolves, forming a deep-blue solution which upon cooling deposits bright-blue needles. These remain to be investigated.

¹ Richards and Shaw: this Journal, 15, 651.

From the mother-liquors decanted from the black crystals may be obtained, at first, $\text{Cu}(\text{NH}_3)_3\text{IC}_2\text{H}_3\text{O}_2$, and, finally, a mixture of $\text{Cu}_3(\text{NH}_3)_{16}\text{I}(\text{C}_2\text{H}_3\text{O}_2)_{16}$ with the coal-black, six-sided crystals already mentioned.¹ These latter crystals are very different in appearance from $\text{Cu}_3(\text{NH}_3)_{10}\text{I}_6$; they will be investigated in the future.

Analyses of $\text{Cu}_3(\text{NH}_3)_{10}\text{I}_6$.

I. 0.2049 gram of the substance yielded ammonia requiring 18.22 cc. of decinormal acid for neutralization, and 0.0352 gram of copper, on electrolysis.

II. 0.2315 gram of the substance required 20.24 cc. of acid and gave 0.0385 gram of copper and 0.2901 gram of argentic iodide.

III. 0.2302 gram of the substance required 20.36 cc. of acid and gave 0.2872 gram of argentic iodide.

IV. 0.2307 gram of the substance required 20.35 cc. of acid.

V. 0.2150 gram of the substance gave 0.0367 gram of copper, on electrolysis.

No.	Copper.	Ammonia.	Iodine.
I.	17.17	15.19
II.	16.63	14.94	67.41
III.	15.11	67.84
IV.	15.07
V.	17.07
	<hr/> 16.96	<hr/> 15.08	<hr/> 67.62

	Calculated for $\text{Cu}_3(\text{NH}_3)_{10}\text{I}_6$.	Found.
Copper	17.00	16.96
Ammonia.....	15.20	15.08
Iodine.....	67.80	67.62
	<hr/> 100.00	<hr/> 99.66

(4) AMMONIC DICUPRIC ACETATE, $\text{NH}_4\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_5\text{H}_2\text{O}$.

Since compounds containing 3 molecules of ammonia, 1 of acetic acid, and 1 atom of chlorine, bromine, or iodine had been proved to exist, it became a matter of interest to discover if it were possible to prepare a salt of the com-

position, $\text{Cu}(\text{NH}_3)_3(\text{C}_2\text{H}_3\text{O}_2)$, in which the halogen is replaced by acetic acid. Many unsuccessful attempts were made to obtain this compound. In the course of these experiments, however, a new double salt of cupric and ammoniac acetates was discovered. 4 grams of cupric acetate, 6 grams of glacial acetic acid, and 20 cc. of alcohol were mixed together, and ammonia-gas was passed into the mixture until the green color just turned to blue. The solution became hot from the absorption of the ammonia, and the cupric acetate dissolved readily. After standing a few hours, many small, bluish-green crystals were deposited, which had the composition given below. The crystals are soluble in water without decomposition, and are fairly permanent in the air.

Analyses of $\text{Cu}_2(\text{NH}_4)(\text{C}_2\text{H}_3\text{O}_2)_5\text{H}_2\text{O}$.

I. 0.2586 gram of the substance yielded an amount of ammonia requiring 5.49 cc. of decinormal acid, and, on electrolysis, gave 0.0717 gram of copper.

II. 0.4303 gram of the substance required 9.40 cc. of acid.

III. 0.2525 gram of the substance gave 0.0703 gram of copper.

IV. 0.2604 gram of the substance required 5.52 cc. of acid and gave 0.0725 gram of copper.

V. 0.3080 gram of the substance gave, on combustion, 0.2970 gram of carbon dioxide.

No.	Copper.	Ammonium.	Acetic acid. $\text{C}_2\text{H}_3\text{O}_2$.
I.	27.73	3.84
II.	3.96
III.	27.84
IV.	27.84	3.84
V.	64.67
Average	27.80	3.88	64.67

	Calculated for $\text{Cu}_2\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)_5\text{H}_2\text{O}$.	Found.
Copper	27.75	27.80
Ammonium	3.94	3.88
Acetic acid.....	64.38	64.67
Water (by diff.)..	3.93	3.65
	100.00	100.00

(5) AND (6) CUPRIAMMONIUM ACETATE.

This salt, discovered by Foerster,¹ may be prepared in an anhydrous condition by allowing an alcoholic solution of cupric acetate to evaporate in the air. Two determinations of the copper present in the blue crystals showed respectively 29.41 and 29.32 per cent., the theoretical being 29.48. The ammonia was found to be 15.68, instead of the theoretical amount 15.82 per cent., corresponding to the formula, $\text{Cu}(\text{NH}_3)_2\text{C}_2\text{H}_3\text{O}_2$.

The crystallized salt, containing $2\frac{1}{2}$ molecules of crystal water, also discovered by Foerster, was prepared in blue, feathery crystals by the evaporation of aqueous ammoniacal cupric acetate. Analysis showed the percentage of copper present to be 24.23 instead of 24.38, and the ammonia to be 13.02 instead of 13.08 per cent. The theoretical values were calculated for the formula $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$.

All of these compounds, as well as many similar obtained from other acids and the substituted ammonias, will be further studied at this laboratory in the near future.

CAMBRIDGE, MASS.

BASSWOOD-OIL.

BY F. G. WIECHMANN.

As, in the literature available, no mention could be found of an oil in basswood (*Tilia Americana*), which the writer recently noticed and extracted, a brief record of the results obtained by an examination of this substance may be of interest.

Two samples of basswood were examined. Both came from the same region, Saginaw, Michigan. They were cut into boards about half an inch in thickness, and about 10 inches in breadth.

Sample No. 1 was sound wood; sample No. 2 presented a peculiar stained appearance and emitted a very strong and disagreeable odor strongly resembling that of rancid butter. On inquiry it was learned that this wood had been kept lying in water for a considerable length of time, and it was evident that some constituent of the wood was undergoing decomposition, which resulted in the formation of some volatile fatty acids.

¹ *Loc. cit.*

In both instances the sample was prepared for analysis by use of a rasp, a fine wood-powder resulting. In the sound wood the whole breadth of the board was evenly worked over; in the other case care was taken to secure the wood-powder principally from the "stained" portions. The oil was extracted in a Soxhlet extraction-tube. 70 grams of wood-powder were used in both instances, and extraction was accomplished by the use of pure ether; the time for extraction was two hours for each charge in the tube. The following results were obtained by examination of the oils, the ether having, of course, been previously removed:

	No. 1.	No. 2.
Yield (expressed in percentage of weight of wood-powder used).....	5.24	3.72 3.70 3.68
Specific gravity $\frac{15^\circ}{15}$ C ...	0.938	—
Congeals at	—10° C.	+5° C.
Saponification-equivalent	315	<div style="display: inline-block; vertical-align: middle;"> $\left\{ \begin{array}{l} \text{Could not be determined; ranged from 152 to 77 inside of a few hours.} \end{array} \right.$ </div>
Iodine-absorption.....	111	
Color	Olive-brown.	Dark-brown.
Heydenreich's reaction..	Yellow and red-brown.	Yellow and red-brown.

Examining the properties of the vegetable oils mentioned in Allen's Commercial Organic Analysis (Vol. II, 2nd Edition), it appears that in some respects basswood-oil resembles cottonseed-oil. The following data on cottonseed-oil are given by Allen:

	Cottonseed-oil.	Basswood-oil.
Specific gravity at 15° C	0.928	
	0.930	0.938
Solidifying-point	1°-10° C.	—10° C.
Iodine-absorption	105-109	111
Saponification-equivalent.....	285-294	315 ¹
Heydenreich's reaction	Reddish-brown.	Yellow and red-brown.

To examine into the nature of the decomposition which the oil obtained from basswood, No. 2, was undergoing, an ether-extract of this oil was saponified by a potassium-hydrate solu-

¹ This high saponification-equivalent is possibly due to the presence of a small amount of resin which was determined in the oil.

tion, twenty hours in all being allowed for the reaction. Water was then added and the mixture placed in a separating-funnel. In this manner a soap solution and an ether solution were obtained. The treatment to which these solutions were subjected, and the data which were secured, are noted in the following scheme:

<p><i>Soap Solution.</i></p> <p>Added sulphuric acid till strongly acid; heated on water-bath for forty-five minutes; filtered while hot and washed with boiling water until reaction was no longer acid.</p>	<p><i>Ether Solution.</i></p> <p>Evaporated to dryness on water-bath; residue oily in character.</p> <p>Hydrocarbons or unsaponified oil.</p> <p>Weight = 0.1616 gr.</p> <p>Congeals at + 2° C.</p>
<p><i>Residue in Filter.</i></p> <p>Dissolved by alcohol-ether (1:1) and evaporated carefully to dryness.</p> <p>Insoluble fatty acids = 0.4951 gr.</p> <p>Specific gravity = 0.898.</p> <p>Congeals at + 5.5° C.</p> <p>Mean combining weight = 342.</p>	<p><i>Filtrate.</i></p> <p>Distilled by live steam passing through for two hours.</p> <p><i>Distillate.</i></p> <p>Neutralized with sodium hydrate (phenolphthalein as indicator); evaporated to dryness and constant weight at 100° C.</p> <p>Volatile fatty acids = 0.1379.</p> <p>Mean combining weight = 92.</p>
<p><i>Residual Solution.</i></p> <p>Neutralized with potassium hydrate (phenolphthalein as indicator); evaporated to dryness on water-bath; extracted residue with ether-alcohol; evaporated to a syrupy solution.</p> <p>Glycerol = 0.2235 gr.</p> <p>Responded to the acrolein and other tests for glycerol.</p>	

These results show that the oil is a glyceride which has suffered partial decomposition, originally induced, most probably, by the presence of mucilaginous or albuminous matter. The volatile fatty acids separated consisted, undoubtedly, in great measure, of butyric acid and its immediate allies.

In conclusion the writer would express his thanks to Messrs. Brainerd and Ziebolz for valuable assistance rendered in securing the analytical data.

COLUMBIA COLLEGE.

NOTE.

A Reagent to replace Hydrogen Sulphide in Qualitative Analysis.

Schiff and Tarugi¹ recommend the use of thiacetic acid as a reagent for the separation of the metals of the second group, thereby avoiding the disagreeable odor of hydrogen sulphide. The acid decomposes with hot hydrochloric acid, giving a very active, nascent hydrogen sulphide, which completely precipitates all the metals of this group. The reagent is made by dissolving 10 cc. of the pure acid in an excess of dilute ammonia, making about 30 cc. ammonium thiacetate solution, which is colored slightly yellow and possesses a weak odor of ammonium sulphide. To the solution to be tested, containing 0.5–1 gram of substance 1–2 cc. of the reagent are added; the solution is then heated to near boiling, but not to the boiling-point. On cooling, there is complete separation of the metals as sulphides. Bismuth, copper, stannous and stannic salts are partially precipitated in the cold, but completely on warming. Lead, mercury, platinum, and gold give red precipitates at first, which are charged to the sulphides on heating. Arsenites and arsenates are separated as the trisulphide. Cadmium is slightly soluble in the hot hydrochloric acid solution, but, on cooling, all of the sulphide is obtained. The chloride, bromide, and iodide of silver are converted into silver sulphide; ferric and chromic salts are instantly reduced to ferrous and chromous salts. Aluminum, manganese, nickel, cobalt, and zinc are not affected, but can be precipitated from an ammoniacal solution. The authors state that they have used the reagent with great satisfaction, and that it has given good results even in the hands of beginners. H. F.

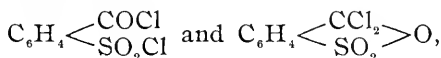
¹ Ber. d. chem. Ges., 27, 3437.

AMERICAN CHEMICAL JOURNAL.

ON THE TWO ISOMERIC CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY IRA REMSEN.

An investigation of the anilides of orthosulphobenzoic acid by C. E. Coates and myself has shown that, when the chloride of the acid is treated with aniline, two products of the formula $C_{19}H_{16}N_2SO_3$ are formed, and that with meta- and para-toluidine similar products are formed. These isomeric substances are well characterized and easily obtained in pure condition. The simplest hypothesis to account for their existence is that they are derived from isomeric chlorides represented by the formulas



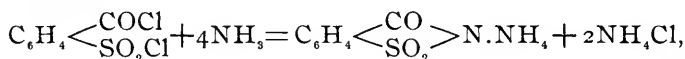
corresponding to the symmetrical and unsymmetrical chlorides of phthalic acid, of which phthalyl chloride is believed to consist.

A subsequent investigation by E. P. Kohler and myself led to the conclusions that the chloride of orthosulphobenzoic acid is, in fact, a mixture of two substances, one a solid at ordinary temperatures, the other an uncrystallizable oil. The crystals melt at about 76° and are identical with those described and analyzed by Remsen and Dohme.¹ It was, further, made

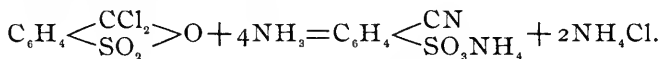
¹ This Journal, II, 341.

extremely probable that the solid chloride is the symmetrical one of the formula $\text{C}_6\text{H}_4\langle\text{COCl}/\text{SO}_2\text{Cl}\rangle$, and that the lower-melting chloride is the unsymmetrical one of the formula $\text{C}_6\text{H}_4\langle\text{CCl}_2/\text{SO}_2\rangle\text{O}$. According to this, one of the anilides is to be represented by the formula $\text{C}_6\text{H}_4\langle\text{CONHC}_6\text{H}_5/\text{SO}_2\text{NHC}_6\text{H}_5\rangle$ and the other by $\text{C}_6\text{H}_4\langle\text{C}(\text{NHC}_6\text{H}_5)_2/\text{SO}_2\rangle\text{O}$.

Still later, A. P. Saunders and myself succeeded in obtaining both the chlorides in crystallized condition and showed that the lower-melting one melts, in fact, at 21.5° – 22.5° . We found that both of the chlorides give ordinary orthosulphobenzoic acid when treated with water; that the symmetrical chloride gives benzoic sulphinide, $\text{C}_6\text{H}_4\langle\text{CO}/\text{SO}_2\rangle\text{NH}$, with ammonia,



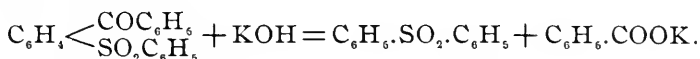
and A. D. Chambers, working in this laboratory, has recently found that the lower-melting or unsymmetrical chloride reacts with ammonia to form the ammonium salt of orthocyanbenzenesulphonic acid, thus,



At the same time some benzoic sulphinide is formed, probably in consequence of a partial transformation of the unsymmetrical into the symmetrical compound. Ammonia acts upon the unsymmetrical chloride much more readily than upon the symmetrical, and upon this fact is based a method, devised by J. E. Bucher, in this laboratory, for the preparation of the symmetrical chloride in pure condition. Other reagents, as water and caustic alkalies, also act first upon the unsymmetrical chloride.

When the mixed chlorides act on benzene and aluminium chloride, a product is first formed which is, apparently, orthobenzoylbenzenesulphone chloride, $\text{C}_6\text{H}_4\langle\text{CO.C}_6\text{H}_5/\text{SO}_2\text{Cl}\rangle$. The

same product is obtained when the pure symmetrical chloride is used. By continued action of benzene and aluminium chloride on the chlorides or on the above-mentioned intermediate product, orthobenzoyldiphenylsulphone, $C_6H_4 \begin{smallmatrix} \text{COC}_6H_5 \\ \text{SO}_2C_6H_5 \end{smallmatrix}$ is obtained. This compound breaks down under the influence of fusing potassium hydroxide, yielding diphenylsulphone and benzoic acid:



The action of phenols upon the chlorides is peculiar and will require further study. Thus far it can only be said that both chlorides, apparently, have a tendency to go over finally to a colored substance like phenolphthalein, but yield crystallized products if the reaction is checked after a few moments. In this way from the mixed chlorides and from the pure solid chloride the normal phenyl ether of orthosulphobenzoic acid, $C_6H_4 \begin{smallmatrix} \text{COOC}_6H_5 \\ \text{SO}_2OC_6H_5 \end{smallmatrix}$, is obtained.

The experimental details are communicated in the following articles.

I. THE ACTION OF ANILINE AND OF THE TOLUIDINES ON ORTHOSULPHOBENZOIC ACID AND ITS CHLORIDE.

BY IRA REMSEN AND C. E. COATES, JR.

An attempt was first made to make the anilide and toluides by heating the aniline and toluidine salts. As these have not previously been prepared brief descriptions of them are first given:

Neutral aniline salt of o-sulphobenzoic acid,

$C_6H_4 \begin{smallmatrix} \text{COOH}(\text{NH}_2C_6H_5) \\ \text{SO}_2\text{OH}(\text{NH}_2C_6H_5) \end{smallmatrix}$.—On adding aniline to a fairly concentrated aqueous solution of the acid, a white voluminous precipitate is thrown down. This precipitate is soluble in alcohol and in considerable hot water. From the solution in hot water, good crystals are readily obtained. They are best obtained pure as follows: Two parts of aniline are added to one part of the acid (in molecular quantities) in aqueous solu-

tion. A small quantity of aniline is then added to ensure excess. The solution is boiled a short time with animal charcoal and filtered while hot. On cooling, transparent crystals separate out, colorless or nearly so, but slowly becoming colored, on standing, in aqueous solution in the light. These crystals are in the form of thick needles or prisms, melt at 165° , and begin to decompose at 185° .

They were analyzed and gave the following results:

I. 0.2605 gram substance gave 0.1606 gram BaSO_4 .

II and III. Nitrogen determinations (Kjeldahl).

IV. 0.2300 gram substance gave 0.4961 gram CO_2 and 0.1083 gram H_2O .

Calculated for $\text{C}_6\text{H}_4\text{SO}_2\text{OH}(\text{NH}_2\text{C}_6\text{H}_5)$		Found.
C	58.76	58.82
H	5.15	5.23
N	7.22	7.28-7.18
S	8.25	8.46

As the aqueous solution of the pure salt changed color on boiling in the air, and as, after boiling some time and crystallizing, the melting-point was altered materially, it was surmised that the salt decomposed on boiling, in part, and the base was carried away in the water-vapor, in which the odor of aniline was distinctly noticed. This was found to be the case and, after boiling several hours, decolorizing with animal charcoal, and allowing the concentrated solution to stand over sulphuric acid, white needles were obtained, which, at 108° , melted partially and gave off water. These needles change color on standing in the air, and on analysis proved to be the acid salt.

Calculated for $\text{C}_6\text{H}_4\text{SO}_2\text{OH}(\text{NH}_2\text{C}_6\text{H}_5) + \text{H}_2\text{O}$		Found.
H_2O	5.75	5.72
N (in dehydrated salt)	4.75	4.71

All the water is given off below 112° . This salt could be obtained readily by adding aniline to the acid, molecule for molecule by weight, and crystallizing from water. It is very soluble in water and as, on boiling the solution, aniline can still be smelt, the second molecule of aniline is probably also carried away slowly in the steam.

The neutral and acid salts of ortho-, meta-, and para-toluidine were prepared in a manner precisely similar to that employed in the case of aniline.

Neutral p-toluidine salt, $C_6H_4 \begin{smallmatrix} \text{COOH}(\text{NH}_2C_6H_4CH_3) \\ \text{SO}_2\text{OH}(\text{NH}_2C_6H_4CH_3) \end{smallmatrix}$, is soluble in hot water and quite difficultly soluble in cold. It forms large thick needles, colorless when pure, but usually straw-colored. Melting-point, 197° .

I. 0.2126 gram substance gave 0.1223 gram $BaSO_4$.

II and III. Nitrogen determinations.

	Calculated for $C_6H_4 \begin{smallmatrix} \text{COOH}(\text{NH}_2C_6H_4CH_3) \\ \text{SO}_2\text{OH}(\text{NH}_2C_6H_4CH_3) \end{smallmatrix}$	I.	Found. II.	III.
S	7.69	7.89
N	6.73	6.61	6.54

Acid p-toluidine salt, $C_6H_4 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{OH}(\text{NH}_2C_6H_4CH_3) \end{smallmatrix} + H_2O$.

—This salt was made by boiling the neutral salt in aqueous solution for some time, or better, by adding molecular weights of *p*-toluidine and the acid in aqueous solution. It consists of colorless needles which lose one molecule of water of crystallization at 100° – 110° . It is very soluble in water.

I. 0.7176 gram of substance lost at 110° 0.0391 gram H_2O .

II. 0.7924 gram of substance lost at 110° 0.0436 gram H_2O .

III. Nitrogen determined by Kjeldahl's method.

	Calculated for $C_6H_4 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{OH}(\text{NH}_2C_6H_4CH_3) \end{smallmatrix} + H_2O$	I.	Found. II.	III.
H_2O	5.51	5.46	5.50
N (in dehydrated salt)	4.53	4.72

Neutral m-toluidine salt, $C_6H_4 \begin{smallmatrix} \text{COOH}(\text{NH}_2C_6H_4CH_3) \\ \text{SO}_2\text{OH}(\text{NH}_2C_6H_4CH_3) \end{smallmatrix}$,

crystallizes in small granular crystals, white, but soon turning pink on exposure to air and light; melting-point, 163.5° .

I. 0.2185 gram substance gave 0.1202 gram $BaSO_4$.

II. Nitrogen determination.

	Calculated for $C_6H_4 \begin{smallmatrix} \text{COOH}(\text{NH}_2C_6H_4CH_3) \\ \text{SO}_2\text{OH}(\text{NH}_2C_6H_4CH_3) \end{smallmatrix}$	Found.
S	7.69	7.55
N	6.73	6.67

Acid m-toluidine salt, $C_6H_4 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{OH}(C_6H_4CH_3NH_2) \end{smallmatrix} + \frac{1}{2}H_2O$.

—Large rhombic crystals, very soluble in water; colorless,

but turning red easily. At 110° it melts nearly completely, at 130° gives off bubbles, and at slightly higher temperature solidifies, melting completely at 164° .

0.0374 gram of acid *m*-salt lost at 104° 0.0156 gram H_2O .

	Calculated for	Found.
	$C_6H_4 < \begin{smallmatrix} COOH \\ SO_2OH \end{smallmatrix} (C_6H_4CH_3NH_2) + \frac{1}{2}H_2O$.	
H_2O	2.83	2.9
N (in dehydrated salt)	4.53	4.54-4.41

Neutral o-toluidine salt, $C_6H_4 < \begin{smallmatrix} COOH(NH_2C_6H_4CH_3) \\ SO_2OH(NH_2C_6H_4CH_3) \end{smallmatrix}$.

—White needles, turning pinkish. Quite soluble in water. Easily decomposed by boiling, forming the acid salt very readily and giving off *o*-toluidine. Melting-point of crystals 127.5° .

0.2172 gram substance gave 0.1196 gram $BaSO_4$.

	Calculated for	Found.
	$C_6H_4 < \begin{smallmatrix} COOH(C_6H_4CH_3NH_2) \\ SO_2OH(C_6H_4CH_3NH_2) \end{smallmatrix}$.	
N	6.73	6.67
S	7.69	7.56

Acid o-toluidine salt, $C_6H_4 < \begin{smallmatrix} COOH \\ SO_2OH \end{smallmatrix} (NH_2C_6H_4CH_3) + \frac{1}{2}H_2O$.

—Crystallizes in white needles, very soluble in water and in alcohol.

I. 0.7280 gram substance lost 0.0209 gram H_2O .

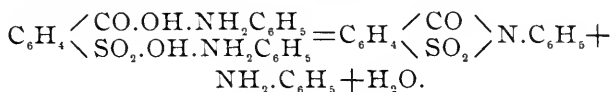
II. 0.6803 gram substance lost 0.0197 gram H_2O .

III. Nitrogen determination.

	Calculated for	I.	Found. II.	III.
	$C_6H_4 < \begin{smallmatrix} COOH \\ SO_2OH \end{smallmatrix} (NH_2C_6H_4CH_3) + \frac{1}{2}H_2O$.			
H_2O	2.83	2.87	2.89	...
N (in dehydrated salt)	4.53	4.4

Having thus obtained the salts of aniline and the toluidines, an attempt was made to obtain the anil and the anilide from the aniline salt by distillation. The aniline salt was heated carefully in a test-tube, but, although at about 185° – 190° a change took place, the only result of higher heating was the production of a carbonized mass from which nothing definite could be extracted. Presuming that the anil could not be distilled, the operation was next carried on thus: About a gram of the salt was placed in a very small retort, so constructed that the substances given off could be collected

and the residue weighed. After heating at 195°–205° for several hours and weighing at intervals, it was found that a continual loss in weight took place, amounting at the last weighing to about 32 per cent., and a colorless liquor distilled over, which proved, on investigation, to be aniline. Now, if the following reaction should take place, thus,



the loss in weight in consequence of the splitting off of aniline and water would amount to 33.25 per cent. On investigating the residue, however, it proved to be a non-crystalline mass which dissolved in considerable hot water to form a red solution, and which could not be obtained except in a gummy state. It was not decomposed by dissolving in sodium hydroxide.

The para-toluidine salt was treated similarly. At 197° it melted, giving off bubbles of something which proved to be para-toluidine. Heated for several hours at 260°–270°, a point was reached at which the reaction seemed complete. The product was, as before, a gum. It melted at about 95°; was soluble in alcohol and in hot water. In ether it was insoluble. On cooling the hot-water solution, it became turbid and an oil separated out—the same thing which had been dissolved, apparently. It appeared not to be capable of distillation at ordinary pressure. Hence a quantity of the gum was placed in a small retort and distilled at a pressure of 15 mm. As before, carbonization took place to a very great extent, but a small quantity of a substance insoluble in water did pass over.

The ortho-toluidine salt behaved in the same way, though it was not distilled at a reduced pressure. A gum always was obtained which, while apparently a definite substance, could not be obtained in crystalline form. This reaction has not as yet been satisfactorily explained, for while the amount lost by the salt corresponds roughly with the theoretical loss in the formation of the anil or the tolil respectively, the anil and the tolil are both substances with very different properties, as will be shown later.

Action of Aniline on the Chloride of Orthosulphobenzoic Acid.

On adding an excess of aniline to some of the chloride in a little water, violent reaction, with heat, ensued. After heating on the water-bath an hour or so, and adding water, an insoluble substance separated out. Filtered off, it dissolved in alcohol, from which it crystallized in white needles melting from 154° – 162° . While it is not absolutely insoluble in hot water, water precipitates it in the cold from concentrated alcoholic solution nearly completely. The same substance was obtained by adding the chloride gradually to an emulsion of aniline in water, keeping cool, and shaking. It is soluble in ether, in alcohol, and in alkalis. Next, the chloride, free from water, was added to aniline, the latter being in excess. After the reaction was over the substance was boiled with water and with hydrochloric acid to remove any excess of aniline. The insoluble residue was crystallized from alcohol after decolorizing with animal charcoal. The crystals were granular, decomposed slowly at temperatures above 250° , were soluble in hot alcohol, and insoluble in water, benzene, and ether.

Fusible Anilide.—After purification, the substance which melted before at 154° – 162° was found to melt at 196° fairly sharply. The crystals were as before, thin white needles. These, on *standing* in contact with the alcoholic solution for some time, change slowly over to large, flat crystals, prismatic, some single, some arranged in radiating clusters. On picking them out mechanically and recrystallizing them, they came down again as needles, and again went over slowly to the prismatic form. This latter form resembles closely the crystals of the infusible substance, but the latter are always terminated, apparently, by basal planes, the former always by obtuse pyramids. This similarity of crystal-form led for some time to the conclusion that the substance was not pure, until, trying the melting-point of the prisms, it was found to be identical with that of the needles. Preliminary analyses for sulphur and nitrogen led to the conclusion that the anilide of orthosulphobenzoic acid had been obtained.

It was then attempted to make it in quantity, but though the conditions were varied in many ways, the yields were uni-

formly poor, never over 5 to 10 per cent. of the theoretical. The best results were obtained as follows :

To an emulsion of an excess of aniline in considerable cold water, the chloride was added slowly, shaking occasionally. The vessel was allowed to stand over night, the supernatant liquid poured off, the residue boiled a few minutes with dilute hydrochloric acid to remove aniline, dissolved in dilute sodium hydroxide in slight excess, filtered, and, when cold, the fairly concentrated solution acidified with hydrochloric acid. The flocculent white precipitate was filtered off, dissolved in alcohol, purified by animal charcoal, and crystallized from hot alcohol. It is not very soluble in cold alcohol, but dissolves on heating. Together with the needles there is frequently formed some of the infusible substance. They can be separated by boiling with ether, which dissolves only the former, or by crystallizing from concentrated solution and decanting the light needles from the heavier prisms which sink to the bottom. The melting-point was not absolutely sharp, but, after two crystallizations, there was only a slight softening below 196° .

I. 0.4254 gram substance gave 0.2856 gram BaSO_4 .

II. 0.2131 gram substance gave 0.1422 gram BaSO_4 .

III. 0.2000 gram substance gave 0.1358 gram BaSO_4 .

IV and V. Nitrogen determinations.

VI. 0.2136 gram substance gave 0.0939 gram H_2O and 0.5165 gram CO_2 .

VII. 0.2152 gram substance gave 0.0952 gram H_2O and 0.5176 gram CO_2 .

Of the portions of substance employed, I, IV, and V were prepared at one time; II, III, and VI at another, and VII at still another.

	Calculated for	I.	II.	III.	Found. IV.	V.	VI.	VII.
	$\text{C}_6\text{H}_4\text{SO}_2\text{NHC}_6\text{H}_5$							
C	64.77	65.49	65.59
H	4.55	4.88	4.92
S	9.09	9.22	9.16	9.32
N	7.95	7.98	7.79

Infusible Anilide.—Attention was now turned to the infusible substance. It was noticed that when several crystals were

heated at 110° a short time to dry them, they lost their transparency and grew chalky. This led to the suspicion that they contained alcohol of crystallization, which proved to be the case. A portion heated at 130° till the weight was constant, was analyzed and found to give, for sulphur and nitrogen, the same figures as the needles had given. A quantity was therefore made in the following manner:

A weighed quantity of aniline was placed in a large, dry test-tube. To this was added, slowly, keeping cool and shaking, such a quantity of the chloride that there should be slightly more than two molecules of aniline for each molecule of the chloride. A violent reaction ensued immediately, and bubbles of hydrochloric acid were given off. In a few minutes the reaction ceased, and the semi-solid mass was heated carefully. More hydrochloric acid was given off. The heating was continued till no more bubbles came off, care being taken not to let the mass get too hot, as then decomposition sets in. The mass was poured on cold porcelain or glass while still fluid, dissolved in alcohol, boiled with animal charcoal, filtered, and crystallized from hot alcohol. The first crystals consisted usually of some needles. These were filtered off. On evaporating the filtrate to a fairly small volume, crystals of the infusible substance were obtained. These were dissolved in hot dilute sodium hydroxide, filtered, and, when cold, precipitated by hydrochloric acid, and the precipitate recrystallized from hot alcohol. The crystals are apparently orthorhombic—though no angles were measured—are always terminated by basal planes, and can be obtained readily, apparently pure, by recrystallizing twice from alcohol. Heated, they lose something at about 160° and turn chalky. At 250° they begin to turn brown. At 270° they begin to melt, with decomposition, and they melt completely to a red liquid at 280° .

About a gram of the crystals was then heated in a large bent tube in a sulphuric-acid bath at 160° . Alcohol was given off, which collected in the cool part of the tube and was recognized both by its smell and by the iodoform reaction.

I. 0.4745 gram substance loses at 130° 0.0553 gram alcohol.

II. 0.5770 gram substance loses at 130° 0.0666 gram alcohol.

In $C_6H_4 \begin{smallmatrix} \text{CONHC}_6H_5 \\ \text{SO}_2\text{NHC}_6H_5 \end{smallmatrix} + C_2H_5OH.$
Calculated for 1 mol. $C_2H_5OH.$

I 1.56

I. Found.
I 1.65

II.
I 1.54

It was necessary to heat to 130° six or eight hours before a constant weight was obtained. At 150° the alcohol was given off more rapidly, but the substance began to turn slightly dark, so the lower temperature was used. The substance from which the alcohol had been driven off was taken for analysis.

I. 0.2706 gram substance gave 0.1811 gram $BaSO_4$.

II. 0.2510 gram substance gave 0.1698 gram $BaSO_4$.

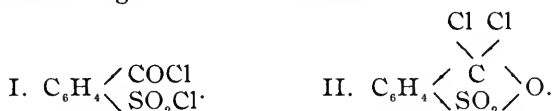
III and IV. Nitrogen determinations (Kjeldahl).

V. 0.2179 gram substance gave 0.0846 gram H_2O and 0.522 gram CO_2 .

VI. 0.2994 gram substance gave 0.126 gram H_2O and 0.7141 gram CO_2 .

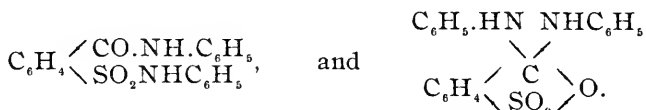
	Calculated for $C_6H_4 \begin{smallmatrix} \text{CONHC}_6H_5 \\ \text{SO}_2\text{NHC}_6H_5 \end{smallmatrix}$	I.	II.	III.	Found. IV.	V.	VI.
C	64.77	65.3	65.05
H	4.55	4.31	4.67
S	9.09	9.19	9.24
N	7.95	8.04	7.89

This substance is formed in greater or less quantity whenever aniline and the chloride are heated together. The needles of the fusible anilide appear to be formed only at low temperatures. What the relation between the two anilides is has not as yet been determined definitely. They both dissolve in alkalis and alkaline carbonates; they are reprecipitated by acids; neither one appears to be a strong enough acid to form a salt when boiled with powdered calcite. In short, they have the same general chemical behavior, while they differ markedly in physical properties, though analysis points to an identity of composition. It is probable that there are two chlorides differing from each other thus:



While of these two formulas, I is usually assigned to the ordinary chloride of orthosulphobenzoic acid, formula II has never been definitely disproved. As is well known, the best

work on the chlorides of succinic and phthalic acids seems to show that in their cases a substance analogous to II must be present as a component of a mixture, if indeed II be not the only proper formula. If this were the case with the chloride of orthosulphobenzoic acid, it is obvious that isomeric anilides could be formed of the formulas



Anil of Orthosulphobenzoic Acid.—In speaking of the infusible anilide, mention was made of some needles which were formed with it and crystallized out first. These were purified and found to melt sharply at 190.5° , and to be insoluble in water, sodium hydroxide, or carbonate. After many experiments the following was decided on as being the best method of preparation :

To a weighed portion of the chloride in a large test-tube, aniline was added in such proportion that there should be slightly more than one molecule of chloride to each molecule of aniline. The proportion should be weighed carefully, as by changing them the products of the reaction are changed also. For example, to 10 grams of chloride add $3\frac{1}{2}$ grams of aniline (theoretical amount required is 3.9 grams). The aniline should be added slowly, and the contents of the test-tube shaken constantly. Violent reaction sets in and subsides in a few moments. Heat carefully over a free flame till no more bubbles of hydrochloric acid are given off, or, perhaps better, heat to the requisite temperature in a sulphuric-acid bath, stirring, and hold at that temperature about half an hour. While still fluid pour out on a piece of cold porcelain. Wash out the test-tube with hot alcohol, dissolve the whole in hot alcohol, boil with animal charcoal, filter, and crystallize. The crystals are long, white flat blades or needles that melt sharply at 190.5° . They are insoluble in water, soluble in hot alcohol, quite difficultly soluble in cold, soluble in hot ether, and difficultly soluble in hot chloroform. They are insoluble in alkalis, but on boiling for some time with dilute sodium hydroxide, they dissolve to a colorless solution,

from which, on acidifying, a new substance is precipitated.

I. 0.209 gram substance gave 0.189 gram BaSO_4 .

II. 0.2542 gram substance gave 0.2273 gram BaSO_4 .

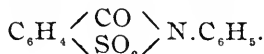
III and IV. Nitrogen determinations (Kjeldahl).

V. 0.2196 gram substance gave 0.4865 gram CO_2 and 0.0771 H_2O .

VI. 0.1736 gram substance gave 0.3891 gram CO_2 and 0.0607 H_2O .

	Calculated for $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{SO}_2\text{NC}_6\text{H}_5$.	I.	II.	III.	Found. IV.	V.	VI.
C	60.23	60.42	61.08
H	3.47	3.90	3.88
S	12.36	12.41	12.28
N	5.41	5.61	5.60

These results show that the substance is the anil,

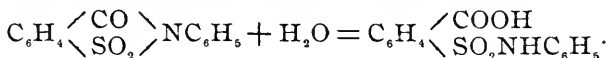


As stated, it was found to be insoluble in alkali. It was noticed, however, that on continued boiling with dilute alkali, a precipitate was obtained on acidifying the filtrate. About a gram of the anil was therefore boiled for an hour with dilute sodium hydroxide and found to dissolve completely. The solution was evaporated to a small volume, and acidified with hydrochloric acid while still hot. A colorless oil separated out, which quickly changed to white, granular crystals. These were soluble in considerable hot water, in alkalies, and alkaline carbonates, and very soluble in alcohol. Acids reprecipitated them from alkaline solution. Analysis gave the following results :

0.1760 gram substance gave 0.1468 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4\langle\text{COOH}\rangle\text{SO}_2\text{NHC}_6\text{H}_5$.	Found.
S	11.55	11.45

It is therefore, as was expected, the anilic acid, formed from the anil by its taking up a molecule of water :



Of course the facts stated do not prove that the aniline residue is in combination with the sulphone group, SO_2 , though

the fact that the acid is not easily soluble in water makes the above view of its constitution probable.

Barium salt of anilic acid, $\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{COO} \\ \diagdown \text{SO}_2\text{NHC}_6\text{H}_5 \end{smallmatrix} \right)_2 \text{Ba} + \text{Aq.}$

—The salt was prepared in the usual way, when an oily mass was obtained, but no good crystals; though on drying at 110° in an air-bath this mass changed to small needles, which appeared to give off water of crystallization, and turned eventually to a white powder. They were soluble in alcohol and in water.

0.1282 gram anhydrous salt gave 0.0432 gram BaSO_4 .

	Calculated for	
	$\left(\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{COO} \\ \diagdown \text{SO}_2\text{NH.C}_6\text{H}_5 \end{smallmatrix} \right)_2 \text{Ba.}$	Found.
Ba	19.88	19.83

On treating the salt with hydrochloric acid, the anilic acid was reprecipitated unchanged. As it evidently had been formed from the anil by hydrolysis some of the acid thus precipitated was heated in a tube in a sulphuric-acid bath. It melted with slight decomposition at about 173° . Heated to over 200° it lost water, which collected in the top of the tube, and was changed to the anil with further slight decomposition. The anil was crystallized out, found to melt at 190.5° , and to correspond in physical properties exactly with the anil from which the anilic acid had been made originally. The circuit from the anil to anilic acid, to barium salt, to anilic acid, and back to anil, was thus completed.

In making the anil and the two anilides, the mother-liquors frequently contained a large amount of a gummy substance. This was soluble in sodium hydroxide, was precipitated by hydrochloric acid, and was nearly insoluble in cold water. It was very soluble in alcohol, but could not be obtained crystalline from any solvent tried. On boiling with strong hydrochloric acid, however, for some time, the gum grew brittle and, finally, quite hard. From this, by crystallization from alcohol, the anil was obtained, melting at 190.5° .

Experiments, similar to those already described, were carried out with para-, meta-, and ortho-toluidines.

Orthosulphobenzo-para-tolil, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{SO}_2 \end{smallmatrix} \text{N.C}_6\text{H}_4\text{CH}_3$.—The

tolil was made precisely as the anil. The yield was better than in the case of the anil, but still not more than 30 per cent. of the theoretical at the best, and usually much less. The crystals consisted of bunches of fine needles, perfectly white, and melting sharply at 195.5° . They are insoluble in water, soluble in hot alcohol, soluble in hot ether, and insoluble in alkalis, by which, however, they are decomposed on continued boiling. They are very difficultly soluble in cold alcohol. They behave in all respects like the corresponding aniline compound.

I. 0.2214 gram substance gave 0.1883 gram BaSO_4 .

II. 0.2017 gram substance gave 0.1746 gram BaSO_4 .

III and IV. Nitrogen determinations (Kjeldahl).

V. 0.2453 gram substance gave 0.5857 gram CO_2 and 0.0952 gram H_2O .

VI. 0.1906 gram substance gave 0.4346 gram CO_2 and 0.0766 gram H_2O .

	Calculated for $\text{C}_6\text{H}_4\text{SO}_2\text{N.C}_6\text{H}_4\text{CH}_3$	I.	II.	Found. III.	IV.	V.	VI.
C	61.54	61.77	62.18
H	4.03	4.31	4.46
S	11.72	11.76	11.88
N	5.13	5.15	5.32

A quantity of the tolil was decomposed by continued boiling with dilute sodium hydroxide. The acid was precipitated by hydrochloric acid, and found closely to resemble the anilic acid in appearance. It is not as soluble in water as the latter, but is easily soluble in alkalis and in alcohol. The barium salt could not be obtained in good crystals, but separated as an oily substance from concentrated solutions. Some of this was dried in the air and between layers of filter-paper.

0.1913 gram of the acid, dried at 110° , gave 0.1531 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4\text{SO}_2\text{NHC}_6\text{H}_4\text{CH}_3$	Found.
S	11.00	10.99

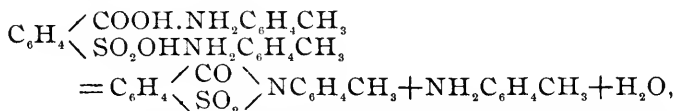
0.1834 gram of air-dried Ba salt lost, on heating at 110° , 0.0128 gram H_2O .

	Calculated for	Found.
	$(C_6H_4 \begin{smallmatrix} \diagup COO \\ \diagdown SO_2NH.C_6H_4CH_3 \end{smallmatrix})_2 Ba + 3H_2O.$	
H_2O	7.06	6.98

0.1706 gram dehydrated Ba salt gave 0.0557 gram $BaSO_4$.

	Calculated for	Found.
	$Ba.2(C_6H_4 \begin{smallmatrix} \diagup COO \\ \diagdown SO_2NHC_6H_4CH_3 \end{smallmatrix}).$	
Ba	19.11	19.21

The salt is decomposed by hydrochloric acid, and the acid itself behaves like the anilic acid, *i. e.*, heated, it melts at about 155° with slight decomposition, and loses water at higher temperatures. A portion of the acid was recovered by treating the barium salt with hydrochloric acid. This was dried and heated in a small test-tube till all the water seemed to have been given off. On recrystallizing a couple of times from alcohol the tolil was recovered pure, melting sharply at 195.5° . Thus in the case of the tolil as well as the anil the circuit was made of taking up water, forming the barium salt, decomposing the barium salt and, by splitting off water, regaining the original substance. In speaking of the attempt to make the tolil by distilling the *p*-toluidine salt under diminished pressure, it was mentioned that a small quantity of substance distilled over in spite of the carbonization. This was preserved, and on recrystallizing it from alcohol it was found to give crystals identical in appearance and in melting-point with the tolil just described. The inference is fair, then, that the tolil is formed by distilling the salt, just as succinil,



but at the temperature necessary for distillation, carbonization takes place to a great extent, probably because of the presence of sulphuric acid residue.

Orthosulphobenzotoluide, (*para*), $C_6H_4 \begin{smallmatrix} \diagup CONHC_6H_4CH_3 \\ \diagdown SO_2NHC_6H_4CH_3 \end{smallmatrix} (?)$.

—This was made by adding to the chloride a little more than

twice the molecular quantity of *p*-toluidine, just as in the case of the anilide. The operation was carried on in exactly the same manner as in that instance. The para-toluide crystallizes out of alcoholic solution in transparent cubes, insoluble in ether, soluble in alkalis, from which they are precipitated by acids, nearly insoluble in hot water, and insoluble in cold water. They contain no alcohol of crystallization, and remain unchanged at 250°. They decompose at higher temperatures.

I. 0.3141 gram substance gave 0.1937 gram BaSO₄.

II and III. Nitrogen determinations (Kjeldahl).

IV. 0.9233 gram substance gave 2.2274 grams CO₂ and 0.4491 gram H₂O. [In this case the combustion was carried on rather more rapidly than usual.]

V. 0.4108 gram substance gave 0.9995 gram CO₂ and 0.2023 gram H₂O.

	Calculated for C ₈ H ₄ CO.NH.C ₆ H ₄ CH ₃ . SO ₂ NHC ₆ H ₄ CH ₃	Found.				
		I.	II.	III.	IV.	V.
C	66.32	65.80	66.35
H	5.27	5.39	5.47
S	8.42	8.47
N	7.37	...	7.18	7.30

An attempt was made to make a toluidine analogous to the fusible anilide. Para-toluidine in excess was added to an emulsion of the chloride in cold water and allowed to stand for some time, the tube being shaken occasionally. It was then boiled, the insoluble residue dissolved in sodium hydroxide, filtered, and precipitated by hydrochloric acid. The precipitate was dissolved in alcohol, and gave, on standing, two kinds of crystals, the cubes just described and needles melting at about 196°. These needles were obtained only in small quantity, and the experiment was not repeated owing to lack of time. They change, on standing in their mother-liquor, to thick prismatic crystals (as the anilide does). As they are quite soluble in chloroform, while the cubes are insoluble, they can be isolated by boiling the two kinds of crystals with chloroform and filtering off the undissolved cubes. When the chloroform was distilled off and the substance crystallized from alcohol, fine prismatic crystals were found. As it resem-

bles the fusible anilide both as to method of formation and its physical properties, that is, in melting without decomposition, being soluble in alkalis and reprecipitated by acids, and being soluble in chloroform and ether—presumably it is the analogous *p*-toluidine compound.

Orthosulphobenzotolil (meta), $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown SO_2 \end{smallmatrix} \diagup N.C_6H_4CH_3$.—

This was made in the same way as the anil and the paratolil. It crystallizes in colorless needles which melt sharply at 147.5° . By crystallizing slowly from alcohol it can be obtained in grains and prisms. Its physical properties are similar to those of the anil and *p*-tolil.

I. 0.1959 gram substance gave 0.1725 gram $BaSO_4$.

II. 0.2609 gram substance gave 0.5920 gram CO_2 and 0.1026 gram H_2O .

III. 0.2184 gram substance gave 0.5001 gram CO_2 and 0.0859 gram H_2O .

	Calculated for $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown SO_2 \end{smallmatrix} \diagup N.C_6H_4CH_3$.	I.	Found. II.	III.
C	61.54	...	61.88	61.53
H	4.03	...	4.36	4.37
S	11.72	12.08

Orthosulphobenzotoluide (meta), $C_6H_4 \begin{smallmatrix} \diagup CONHC_6H_4CH_3 \\ \diagdown SO_2NHC_6H_4CH_3 \end{smallmatrix} + C_2H_5OH$.—By adding to the chloride slightly more than twice the molecular quantity of meta-toluidine, and carrying out the operation as in the case of the infusible anilide and toluidine, the meta-toluide was obtained in short prismatic crystals, not melting at 250° , and with physical properties like those of the infusible anilide. It contains one molecule of alcohol of crystallization, which it loses slowly at 120° . The substance from which the alcohol has been driven off is somewhat hygroscopic.

1.0272 gram substance lost 0.1130 gram of alcohol at 120° :

C_2H_5OH	$C_6H_4 \begin{smallmatrix} \diagup CO.NHC_6H_4CH_3 \\ \diagdown SO_2.NHC_6H_4CH_3 \end{smallmatrix} + C_2H_5OH$.	Found.
	10.8 per cent.	11 per cent.

I. 0.2695 gram *m*-toluide without alcohol of crystallization gave 0.1668 gram $BaSO_4$.

II. 0.1703 gram gave 0.4154 gram CO₂ and 0.0867 gram H₂O.

	Calculated for $C_6H_4 \begin{matrix} \text{CO.NHC}_6H_4CH_3 \\ \text{SO}_2.NHC_6H_4CH_3 \end{matrix}$	Found.
C	66.32	66.52
H	5.26	5.60
S	8.42	8.49

As in the case of the anilide, the alcohol of crystallization was driven off, collected, and identified both by its odor and by the iodoform reaction.

The attempt to make the isomeric meta-toluide, analogous to the anilide melting at 195°–196°, was carried out as follows: The chloride was added slowly to an emulsion of an excess of the *m*-toluidine in ice-water, with constant shaking. The mixture was allowed to stand several hours, then washed with hydrochloric acid, and the residue dissolved in sodium hydroxide. It was boiled till most of the smell of *m*-toluidine had disappeared; filtered and precipitated with hydrochloric acid. A gum separated out which was somewhat soluble in water. It dissolved in alcohol very easily. On carefully adding water to the alcoholic solution, a crystalline deposit was obtained. This was filtered off, washed, and dissolved in alcohol, from which it crystallizes well in large grains, melting quite sharply at 161.5°–162.5°. These crystals were soluble in alcohol, ether, and chloroform. From alkaline solution the substance was precipitated, unchanged by acids. It behaved in every way like the anilide melting at 195°–196°, and the substance which was presumably the fusible *p*-toluide. Owing to lack of time only sulphur could be determined.

0.1625 gram substance gave 0.0978 gram BaSO₄.

	Calculated for $C_6H_4 \begin{matrix} \text{CO.NHC}_6H_4CH_3 \\ \text{SO}_2.NHC_6H_4CH_3 \end{matrix}$	Found.
S	8.42	8.23

It is therefore, in all probability, isomeric with the infusible *m*-toluide. This isomerism can be explained in the same manner as was that of the anilides.

Orthosulphobenzotolil (*ortho*), $C_6H_4 \begin{matrix} \text{CO} \\ \text{SO}_2 \end{matrix} \text{N.C}_6H_4CH_3$.—

This was made in the same manner as the anil and the other

tolils. It is more soluble in alcohol than any of them, and was obtained in short, thick needles or plates, melting not very sharply at 172° – 175° after several recrystallizations. It had the same general physical properties as the homologous compounds.

I. 0.1982 gram substance gave 0.1657 gram BaSO_4 .

II. 0.1856 gram substance gave 0.1543 gram BaSO_4 .

III. 0.3455 gram substance gave 0.7792 gram CO_2 and 0.1278 gram H_2O .

IV. 0.3357 gram substance gave 0.757 gram CO_2 and 0.1273 gram H_2O .

	Calculated for $\text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix}\text{--NC}_6\text{H}_4\text{CH}_3$.	Found.			
		I.	II.	III.	IV.
C	61.54	61.51	61.50
H	4.03	4.11	4.21
S	11.72	11.47	11.42

Orthosulphobenzotoluide (ortho), $\text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CO.NH.C}_6\text{H}_4\text{CH}_3 \\ \text{SO}_2\text{NHC}_6\text{H}_4\text{CH}_3 \end{smallmatrix} + 2\text{C}_2\text{H}_5\text{OH}(?)$.—On attempting to make this by following the method used for the other toluids, nothing was at first obtained. It was made, finally, in the following manner: A slight excess of *o*-toluidine was added to the chloride and heated as in the case of the anilide. On crystallizing from alcohol, after boiling with animal charcoal, some crystals of the *o*-tolil (melting-point, 172° – 174°) were obtained. These were filtered off, the mother-liquor evaporated to a small volume, and the gummy mass dissolved in a little sodium hydroxide. Some tolil was left undissolved and filtered off. After boiling the sodium-hydroxide solution until no more odor of toluidine was noticed, and acidifying with hydrochloric acid, a considerable quantity of granular crystals separated out on cooling. These were soluble in considerable hot water and easily soluble in alcohol. From the alcoholic solution, water precipitates the substance as a liquid, which gradually becomes crystalline. From *very* concentrated alcoholic solutions prismatic crystals are deposited, resembling in form those of the infusible anilide. On standing even a short time in the air they give off alcohol of crystallization, and

effloresce, turning chalky and crumbling under the touch. On this account the figures for alcohol of crystallization were not close, but there are probably two molecules. The crystals do not melt without decomposition, and they behave like the infusible anilide. The substance from which the alcohol had been driven off (at 120°) gave the following analytical results:

I. 0.3418 gram substance gave 0.2146 gram BaSO₄,

II. Nitrogen determination (Kjeldahl).

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{CO.NHC}_6\text{H}_4\text{CH}_3 \\ \text{SO}_2\text{NHC}_6\text{H}_4\text{CH}_3 \end{cases}$	Found.
S	8.41	8.62
N	7.37	7.34

An estimation of sulphur was made in the crystals precipitated from alkaline solution by acid.

0.2148 gram gave 0.1285 gram BaSO₄.

	Calculated.	Found.
S	8.42	8.21

A combustion was made of a small quantity of somewhat impure material, which was all there was at hand. Owing to limited time, a fresh supply of pure substance could not be made.

0.2395 gram substance (impure), from which alcohol of crystallization had been driven off, gave 0.5879 gram CO₂ and 0.1178 gram H₂O.

	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{CO.NHC}_6\text{H}_4\text{CH}_3 \\ \text{SO}_2\text{NHC}_6\text{H}_4\text{CH}_3 \end{cases}$	Found.
C	66.32	66.93
H	5.26	5.46

An attempt was made to prepare the isomeric ortho-toluide corresponding to the fusible anilide and meta-toluide, but nothing definite was obtained owing, possibly, to the fact that the substance was too soluble to crystallize from ethyl alcohol, which was the solvent employed. The same method was employed as in the case of the anilide, *i. e.*, shaking the chloride and the toluidine together in cold water, but only the infusible toluide just described was obtained.

Summary.

1. The aniline and toluidine salts, both acid and neutral, of orthosulphobenzoic acid were made and analyzed.

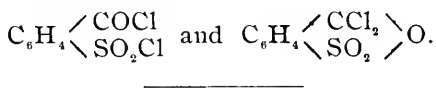
2. The neutral salt is decomposed on boiling in aqueous solution, giving off the base and forming first the acid salt, and then, possibly, the free acid.

3. While on distillation the salts are, for the most part, carbonized, nevertheless, the para-tolil, at least, is formed in small quantity by distilling the neutral salt at 15 mm. pressure. The neutral salts, moreover, on being heated for some time to about 230°, give off the base in part, and form a gum which may be the unsymmetrical anil or tolil.

4. The anil and the tolils are formed by the action of the chloride on the bases, molecule for molecule.

5. They take up water when boiled with dilute alkalies and form the anilic and tolilic acids, which form, in turn, definite salts, and revert to the anil or tolil respectively when heated above 200°, losing water.

6. The formation of two anilides of markedly different physical properties, and the formation, in the same manner, of two meta-toluides, and probably two para-toluides, tends to confirm the view that the chloride of orthosulphobenzoic acid is a mixture of the two compounds



II.—FURTHER STUDY OF THE ACTION OF ANILINE ON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY IRA REMSEN AND E. P. KOHLER.

As the results of the investigation by Remsen and Coates made it appear probable that the chloride of orthosulphobenzoic is a mixture of two isomeric substances, the work was continued in the hope of obtaining further evidence. The chloride was prepared in the usual manner from the pure acid potassium salt of the acid. After heating on the water-bath for some time, the mass was poured into a large quantity of cold water. On separating it from this it was washed with

almost boiling water until neither the last washings nor a solution obtained by decomposing a small quantity of the oil with boiling water gave any reaction for phosphoric acid. Finally, it was dried over concentrated sulphuric acid and solid caustic potash. Thus prepared, the product is a colorless oil which assumes a waxy consistency after standing over sulphuric acid for some time.

Attempts to separate the constituents of the chloride by means of ether, chloroform, and benzine, were not successful. Well-formed needles were obtained together with an oil, but the products were of such a character as to make their investigation unpromising. When the chloride is treated with cold water, it gradually changes to a network of crystals imbedded in an oily matrix. This is the simplest method of obtaining the crystals. A layer of the oil, just thick enough to cover the bottom of the vessel used, is covered with cold water and allowed to stand in a cool place until no further increase in the amount of crystals formed is observed. The water and oil are then rapidly poured off, and the crystals which cling to the bottom of the vessel washed, first with a jet of cold water and, finally, with a little ether.

If the crystals obtained by any of the above methods are dissolved in ether, chloroform, or benzine, they crystallize out again, readily and completely.

Neither the benzine nor the ethereal solution gives any sign of decomposition. The result is the same whether the temperature is kept constant or not, or whether the evaporation is slow or rapid. After one recrystallization the crystals melt sharply at 76° and resolidify on cooling.

These crystals undoubtedly are the substance described by Remsen and Dohme¹ as orthosulphobenzoyl chloride. An analysis gave the following results :

- I. 0.2015 gram substance gave 0.2393 gram AgCl.
- II. 0.2205 gram substance gave 0.2621 gram AgCl.

	Calculated for $C_7H_7SO_2Cl_2$.	I.	Found.	II.
Cl	29.65	29.46		29.4

These facts are given in detail to show that the product of the action of phosphorus pentachloride upon salts of ortho-

¹ This Journal, II, 332.

sulphobenzoic acid does not act towards solvents like a single individual. The peculiarities observed are most readily explained on the assumption that the product is composed of two compounds, one a solid melting at 76° , the other an oily liquid capable of dissolving the solid. As this view is supported by the chemical behavior of the product, the terms *liquid* and *solid* will hereafter be used to distinguish the two constituents of the mixture, while the term *mixed chlorides*, or simply *chloride*, will be used to designate the entire product.

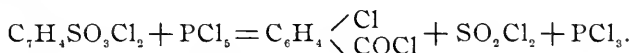
Behavior of the Chloride on Heating.—An accidental modification of the conditions while preparing some of the chloride showed that it is easily decomposed either by heat or an excess of phosphorus pentachloride. A quantity of acid potassium orthosulphobenzoate was treated with a considerable excess of phosphorus pentachloride, warmed on the water-bath for some time, and then allowed to stand over night. In the morning the chlorides of phosphorus were distilled off as completely as possible at 120° , and the residue washed with cold water. A very decided odor resembling that of benzoyl chloride was observed. When hot water was added to the dark-colored liquid it solidified almost completely, the odor of benzoyl chloride disappearing at the same time. The mass was dissolved in boiling water, filtered in order to remove a small quantity of insoluble tarry matter, boiled with animal charcoal, and allowed to crystallize. The liquid became filled with a mass of yellowish white needles, which, after recrystallization from water, were of a pure white color and melted sharply at 137° . By their melting-point and other physical properties they were easily identified as orthochlorbenzoic acid. This showed that the chlorides of orthosulphobenzoic acid yield a chlorbenzoyl chloride much more readily than the corresponding meta- and para-compounds. As this might affect the purity of the chloride used in subsequent experiments, the conditions under which this decomposition takes place were carefully studied, with the following results:

When heated alone the chloride begins to decompose slowly at 150° . The decomposition increases in rapidity as the temperature is raised until the boiling-point of chlorbenzoyl chlo-

ride is reached. The decomposition is probably represented by the equation



while secondary reactions give rise to a considerable quantity of tarry material. The decomposition is not affected by the presence of phosphorus oxychloride. Phosphorus pentachloride greatly assists the decomposition, lowering the initial temperature to 100° , and diminishing the amount of resinous material formed. The reaction is probably expressed by the equation



In the reaction between phosphorus pentachloride and salts of orthosulphobenzoic acid, a product free from orthochlorobenzoic acid can be readily obtained by avoiding an excess of phosphorus pentachloride and a temperature above 100° .

I. *Action of Aniline on the Mixed Chlorides in the Presence of Water.*—32 grams of aniline were added to 20 grams of the chloride in an emulsion in a liter of water. The mixture was shaken until no more aniline was taken up. The excess of aniline was then distilled off in a current of steam, the liquid removed by filtration, and the insoluble residue dried, powdered, and extracted with boiling ether. The ethereal solution, on evaporation, gave only the substance described by Remsen and Coates as the fusible anilide of orthosulphobenzoic acid.

The residue from the ethereal extract was the infusible anilide of orthosulphobenzoic acid, practically pure. The filtrate from the part insoluble in water was evaporated to a small volume and allowed to cool. A considerable quantity of pure infusible anilide crystallized out. On further evaporation of the mother-liquor a mixture was obtained, which it was impossible to separate by recrystallization. The mother-liquor was therefore evaporated to dryness, the residue powdered and extracted with boiling ether. The ethereal solution contained only aniline hydrochlorate. The residue insoluble in ether gave, on recrystallization from water, a new substance which, as will be shown later, is the aniline salt of orthosulph-

anilidobenzoic acid. The proportion in which the different substances derived from orthosulphobenzoyl chloride were obtained is as follows:

18.7 grams of infusible anilide, corresponding to 64.5 per cent. of the chloride.

6.4 grams of fusible anilide, corresponding to 2.2 per cent. of the chloride.

2.8 grams of the salt, corresponding to 9 per cent. of the chloride.

Not accounted for, 4.5 per cent. of the chloride.

II. *Action of Aniline on the Dry Mixed Chlorides.*—Aniline was slowly added to 20 grams of chloride until a decided odor of aniline remained after the mixture had been warmed on the water-bath for some time. Water was then added to the mass, and the excess of aniline distilled off in a current of steam. The remainder was evaporated to dryness and the residue extracted with ether. The ethereal solution contained only orthosulphobenzanil and a small quantity of aniline hydrochloride. The residue insoluble in ether was extracted with a boiling mixture of alcohol and ether. This solution contained the infusible anilide, which separated out almost completely on cooling, and some aniline hydrochloride which remained in solution. The small portion insoluble in the mixture gave, on recrystallization from water, the aniline salt of sulphanilidobenzoic acid. The relative amounts in which the different substances are formed are as follows:

19.2 grams of infusible anilide, corresponding to 66.2 per cent. chloride.

5.3 grams of anil, corresponding to 24.5 per cent. chloride.

2 grams of salt, corresponding to 6.5 per cent. chloride.

Not accounted for, 3.2 per cent. chloride.

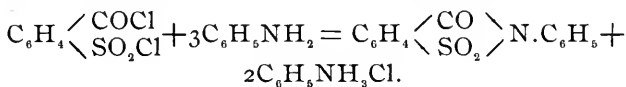
III. *Action of Aniline upon the Pure Solid Chloride in the Presence of Water.*—2 grams of the crystalline chloride were powdered and suspended in water. Aniline was then added until it was no longer acted upon. The reaction was very slow, requiring several days for its completion. The product was treated as in I (page 333). Only the fusible anilide was obtained. The yield was 98 per cent. of the theoretical. This experiment was repeated a number of times, but nothing except the fusible anilide was ever obtained.

IV. *Action of Aniline on the Dry Solid Chloride.*—About 2 grams of the solid chloride were melted on the water-bath and aniline added until it was in slight excess. The product was treated as in II (page 334). Only the anil and aniline hydrochlorate were obtained. This experiment was also performed a number of times with invariably the same results.

V. *Action of Aniline on the Purest Liquid Chloride Obtained.*—Portions of the chloride from which the solid constituent had been removed, as completely as possible, by means of chloroform were treated with aniline as in I and II. The products were the same as those obtained from the mixed chlorides.

The facts established by means of these experiments, as well as those revealed by the study of the behavior of the chloride towards solvents, lead to the conclusion that it is a mixture of two substances, and that the isomerism observed in the anilides, whatever its nature, is to be referred to similar relations between these two chlorides. The experiments show conclusively that the solid chloride gives no infusible anilide, no matter under what conditions aniline is allowed to react with it, and that the infusible anilide is invariably formed when aniline reacts with a chloride which contains some of the liquid material, the amount of infusible anilide formed, increasing in the proportion that the solid chloride is removed from the mixture.

The Anil.—Orthosulphobenzanil, as previously mentioned, is the only derivative of orthosulphobenzoic acid obtained by the action of aniline on the dry solid chloride. The reaction is quantitative, aniline hydrochloride being the other product. It may therefore be expressed by the equation



It has been shown that the anil is formed in small quantities by the action of dry aniline upon the mixed chlorides, and it will be shown later that it is also formed by the action of phosphorus pentachloride upon orthosulphanilido-benzoic acid.

The general properties of the anil have been described by

Remsen and Coates. It is difficult to get it in an absolutely pure condition. When recrystallized from alcohol it invariably softens slightly at 180° – 185° , and then melts completely at 190° . The best results were obtained by recrystallizing it from a mixture of alcohol and ether. A specimen prepared in this way gave, on analysis, the following results :

I. 0.2103 gram substance gave 0.4633 gram CO_2 and 0.0760 gram H_2O .

II. 0.2181 gram substance gave 0.4809 gram CO_2 and 0.0725 gram H_2O .

III. 0.1085 gram substance gave 0.0988 gram BaSO_4 .

IV. 0.1562 gram substance gave 0.1403 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4\text{SO}_2\text{N.C}_6\text{H}_5$	I.	II.	Found.		V.	VI.
				III.	IV.		
C	60.23	60.08	60.13
H	3.47	4.02	3.69
S	12.36	12.41	12.51
N	5.41	5.36	5.32

In its chemical properties the anil closely resembles the mother-substance, benzoic sulphinide. When boiled with dilute hydrochloric acid it gradually goes into solution. On evaporating the solution to a small volume, long, colorless needles are obtained, which, as shown by analysis, consist of the acid aniline salt of orthosulphobenzoic acid, which was obtained by Remsen and Coates by the action of one molecule of aniline upon one molecule of orthosulphobenzoic acid. A determination of the sulphur in the compound gave the following results :

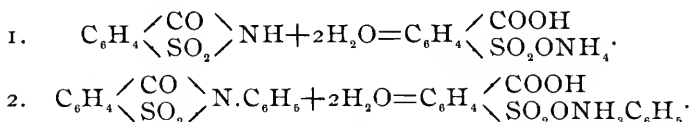
I. 0.2105 gram substance gave 0.1618 gram BaSO_4 .

II. 0.1420 gram substance gave 0.1108 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4\text{SO}_2\text{ONH}_3\text{C}_6\text{H}_5$	I.	Found.	II.
S	10.52	10.6		10.65

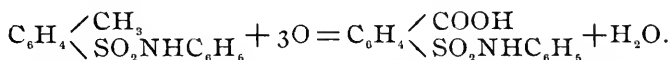
The nature of the substance is also shown by its behavior toward alkalis. When caustic potash solution is added to the solution of the salt, aniline is liberated at once, and if the solution is then strongly acidified with concentrated hydrochloric acid, the acid potassium salt of orthosulphobenzoic acid crystallizes out.

The action of hydrochloric acid upon orthosulphobenzanil is therefore analogous to the action of the same reagent upon benzoic sulphinide:



The anil is insoluble in cold dilute alkalies, but goes into solution on boiling. From this solution mineral acids precipitate an acid which passes back into the anil on heating. This acid was also prepared by another method, which shows its structure and that of the anil derived from it.

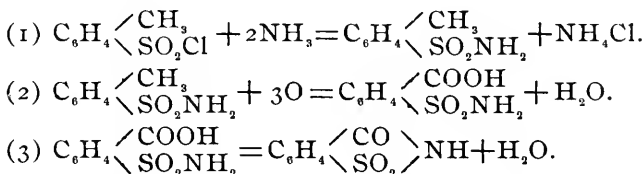
When orthotoluenesulphone chloride is treated with aniline, orthotoluenesulphonanilide is obtained. In this compound the aniline residue must be in combination with sulphur. By oxidation with potassium permanganate it is converted into orthosulphanilidobenzoic acid, thus,



This acid, in which the aniline must likewise be united with sulphur, was found to be identical with the acid obtained by the action of alkalies upon the anil. On heating, it passes into the anil according to the equation



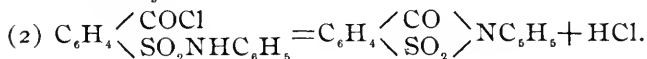
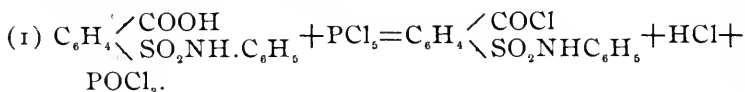
These transformations are analogous to those by which benzoic sulphinide was first obtained by Remsen and Fahlberg¹:



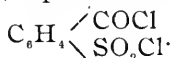
The passage from the anilic acid to the anil is, however, by no means as easy as the corresponding passage to the sulphinide. The transformation by heating is not satisfactory, as at the high temperature required other decompositions take place to a considerable extent. With the aid of phosphorus penta-

¹ This Journal, I, 426.

chloride the passage can be readily and cleanly made at the ordinary temperature. For this purpose the anilic acid is dissolved in dry chloroform, and the calculated amount of phosphorus pentachloride added to the solution. The evolution of hydrochloric acid begins at once and the reaction is complete in a few minutes. By distilling off the chloroform and chlorides of phosphorus as completely as possible under diminished pressure, and crystallizing the residue from a mixture of alcohol and ether, pure orthosulphobenzanil is obtained. It was impossible to obtain an intermediate chlorine-product, although the reaction probably takes place in two stages, as represented by the equations:



These reactions leave little doubt that the substance is the symmetrical anil of orthosulphobenzoic acid, and, as it is formed quantitatively from the solid chloride, the natural conclusion is that the latter is the symmetrical dichloride of orthosulphobenzoic acid, represented by the formula



It has also been shown that the fusible anilide is the only product obtained by the action of aniline upon the solid chloride in the presence of water. This leads to the conclusion that the fusible anilide is the symmetrical dianilide of orthosulphobenzoic acid, a conclusion which, as will be shown later, is confirmed by the chemical properties of the substance.

Reaction of the Anil with Aniline.—The anil readily dissolves in cold aniline. From this solution the anil is obtained unchanged if the aniline is distilled off in a current of steam. If the solution is boiled for a few hours before the aniline is distilled off with steam, the residue, when crystallized from alcohol, gives pure fusible anilide, in calculated quantity. This experiment was repeated a number of times under modified conditions, in order to determine whether the infusible anilide could in any way be formed by the direct addition of aniline

to the symmetrical anil. Nothing but the fusible anilide was ever obtained. The reaction is, doubtless, analogous to that observed by Remsen and Dohme¹ in the case of benzoic sulphimide :



The Fusible Anilide.—This substance is formed quantitatively by the action of aniline upon the solid chloride in the presence of water. It is also formed in small quantity by the action of aniline upon the mixed chlorides in the presence of water, and, in calculated amounts, by the direct addition of aniline to the anil. It is readily obtained in pure form by recrystallization from alcohol or ether. A complete analysis gave the following results :

0.1347 gram substance gave 0.3200 gram CO_2 and 0.0559 gram H_2O .

0.1842 gram substance gave 0.4383 gram CO_2 and 0.0808 gram H_2O .

0.2008 gram substance gave 0.1344 gram BaSO_4 .

0.2102 gram substance gave 0.1417 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CONHC}_6\text{H}_5 \diagdown \\ \diagdown \text{SO}_2\text{NHC}_6\text{H}_5 \diagup \end{array}$	I.	II.	Found. III.	IV.	V.	VI.
C	64.77	64.77	64.9
H	4.55	4.67	4.95
S	9.09	9.22	9.26
N	7.95	7.89	7.86

The chemical behavior of this substance is, throughout, that of an acid anilide. When boiled with dilute hydrochloric acid it gradually goes into solution. From this solution there is obtained, on concentration, first, a mass of highly colored needles, and then a smaller quantity of thin, glistening plates. The needles, on recrystallization from water, are obtained colorless, and, as shown by analysis and comparison, are composed of the acid aniline salt of orthosulphobenzoic acid, which was also obtained by similar treatment of the anil. A

¹ *Loc. cit.*

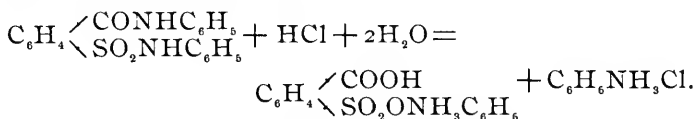
determination of the sulphur contained in the compound gave the following results:

0.1614 gram substance gave 0.1270 gram BaSO_4 .

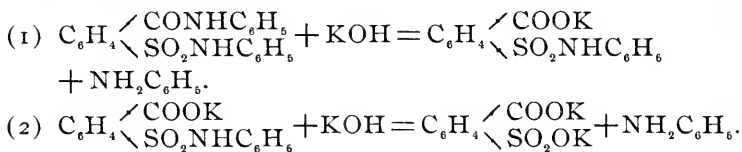
0.1410 gram substance gave 0.1110 gram BaSO_4 .

S	Calculated for	Found.	
	$\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{COOH} \\ \diagdown \text{SO}_2\text{NH}_2\text{C}_6\text{H}_5 \end{smallmatrix}$	I.	II.
	10.76	10.8	10.86

The leaflets, on recrystallization from water, melted at 192° , gave off aniline on addition of cold alkali, and were, undoubtedly, aniline hydrochlorate. The decomposition with hydrochloric acid is therefore represented by the equation



The anilide readily dissolves in dilute alkalis, and crystallizes out again unchanged if this solution is neutralized with dilute acids. If the solution is boiled for a short time and then acidified, the orthosulphanilidobenzoic acid, previously obtained by the action of alkalis on orthosulphobenzanil, and by the oxidation of orthotoluenesulphonanilide, is obtained. It is readily identified by its melting-point and crystal form. Part of the acid is generally decomposed by the alkali, as a small quantity of acid potassium orthosulphobenzoate is also obtained. If a strongly alkaline solution is boiled for a sufficiently long time (six to eight hours were generally found sufficient), the decomposition into the potassium salt of orthosulphobenzoic acid is complete, all the aniline passing off with the steam. With alkalis, therefore, the fusible anilide is decomposed in two stages, as represented by the equations:



These decompositions, both with acids and alkalis, are characteristic of acid anilides, while the fact that the decomposition with alkalis takes place in two stages is most readily

explained on the supposition that the two aniline residues bear different relations to the molecule. This leads to the structure $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CONHC}_6\text{H}_5 \\ \diagdown \text{SO}_2\text{NHC}_6\text{H}_5 \end{smallmatrix}$, which represents one aniline residue as united with carbon and the other with sulphur. As will be shown later, it is much more difficult to saponify a sulphonanilide than the corresponding carbonic anilide. It is, therefore, to be expected that a dianilide with this structure would, under proper conditions, lose, first the aniline residue combined with carbon, and eventually all the aniline. That this takes place with the fusible anilide follows from the fact that the product obtained in the first stage of the action of alkalis undoubtedly has the aniline combined with sulphur.

Taking all these facts into consideration—the formation from the chloride which, under other conditions, gives only symmetrical orthosulphobenzanil; the ease with which it passes into the same anil by loss of aniline, and is formed from the anil by addition of aniline; the chemical behavior, which is, throughout, that of an acid anilide; and its decomposition into orthosulphobenzoic acid and aniline in two stages—there can be no reasonable doubt that the fusible anilide is the symmetrical dianilide of orthosulphobenzoic acid, as represented by the formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CONHC}_6\text{H}_5 \\ \diagdown \text{SO}_2\text{NHC}_6\text{H}_5 \end{smallmatrix}$.

The Infusible Anilide.—This substance is invariably the main product of the action of aniline upon the mixed chlorides. The best way to purify it is to recrystallize it from boiling water, from which it is obtained in colorless orthorhombic prisms. An analysis of the substance purified in this way gave the following results:

- I. 0.2802 gram substance gave 0.1867 gram BaSO_4 .
- II. 0.2051 gram substance gave 0.1376 gram BaSO_4 .
- III. 0.1231 gram substance gave 0.2933 gram CO_2 and 0.053 gram H_2O .
- IV. 0.1300 gram substance gave 0.3097 gram CO_2 and 0.0573 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{16}\text{SO}_3\text{N}_2$.	I.	II.	III.	Found. IV.	V.	VI.
C	64.77	64.98	64.8
H	4.57	4.71	4.91
S	9.09	9.15	9.22
N	7.95	7.96	7.89

In its chemical conduct the infusible anilide is characterized by remarkable resistance to the action of most reagents. When boiled with hydrochloric acid of the same strength as that used to transform the fusible anilide and the anil into acid aniline orthosulphobenzoate, it goes into solution, but crystallizes out again unchanged on cooling. The result is the same no matter what the strength of the acid used may be, or at what temperature the two are heated together. In a final experiment the anilide was heated in a sealed tube with concentrated hydrochloric acid, and the temperature kept above the boiling-point of mercury for ten hours. It crystallized out unchanged on cooling.

It also dissolves very readily in dilute alkalies, but no matter how long the alkaline solution is boiled, or how concentrated may be the alkali used, or whether in water or alcoholic solution, acids invariably reprecipitate the unchanged anilide.

The anilide also dissolves in concentrated nitric acid. From this solution, and from its solution in fuming nitric acid, it crystallizes unchanged on dilution, but it is completely decomposed by boiling with fuming nitric acid.

The first decomposition of the substance was effected by means of benzoyl chloride. A small quantity was boiled with benzoyl chloride until it was completely dissolved. The excess of the chloride was then removed as completely as possible by distillation under diminished pressure, and the residue boiled with water. The product, difficultly soluble in water, was crystallized from alcohol, and found to be benzanilide. Its identity was established by means of its melting-point and by comparison with a specimen of benzanilide prepared by the action of aniline on benzoyl chloride. The other product could not be isolated. It was found, however, that if aniline is added to this product the infusible anilide is reformed, indicating that the action of benzoyl chloride, in all probability, consists in replacing at least one of the aniline residues with chlorine. In any case, the formation of benzanilide shows that the infusible anilide contains aniline residues intact, and that no such deep-seated changes are involved in its formation as its indifference to reagents might lead one to suppose.

Phosphorus pentachloride and phosphorus oxychloride likewise react with the anilide, the former in chloroform solution, the latter directly. The products of the reaction are still under investigation.

The experimental evidence thus far obtained does not justify any conclusion as to the structure of the infusible anilide.

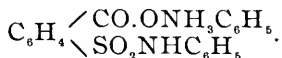
Aniline Salt of Orthosulphanilidobenzoic Acid.—This is the fourth aniline derivative of orthosulphobenzoic acid formed by the action of aniline upon orthosulphobenzoyl chloride. Its formation in small quantities is doubtless due to secondary reactions. It crystallizes in long, colorless prisms which, when moist, readily assume a reddish tint in the air; is readily soluble in water and alcohol, difficultly soluble in ether. A sulphur determination gave the following results:

0.1850 gram substance gave 0.1178 gram BaSO₄.

0.1624 gram substance gave 0.1042 gram BaSO₄.

Calculated for		Found.	
$C_6H_4 \begin{cases} CO.ONH_3C_6H_5 \\ SO_2NHC_6H_5 \end{cases}$		I.	II.
S	8.66	8.75	8.81

The salt was also prepared by adding a calculated quantity of aniline to orthosulphanilidobenzoic acid. This method shows that its structure is represented by the formula



Orthotoluenesulphonanilide.—This substance was first prepared by Müller, who gives its melting-point, 136°, but no analysis or further description. As it played an important part in the investigations described above, it was thought desirable to study it somewhat in detail. It was prepared by the action of aniline upon orthotoluenesulphone chloride. A slight excess of aniline was added to the chloride, the mixture warmed on the water-bath, and the excess of aniline removed by distillation in a current of steam. The residue was recrystallized from a mixture of alcohol and water, and the anilide thus easily obtained in a pure state. It melts sharply at 136°, the melting-point given by Müller. It crystallizes in large, colorless prisms, which generally have a tabular development and belong to the orthorhombic system. It is readily soluble in cold alcohol, while it practically mixes in all proportions

with hot alcohol. It is difficultly soluble in ether and water. Heated with water it melts to a heavy oil which, on cooling, solidifies to a crystalline mass. A determination of sulphur and nitrogen gave the following results :

0.1642 gram substance gave 0.1552 gram BaSO_4 .

0.1428 gram substance gave 0.1362 gram BaSO_4 .

Calculated for $\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{NHC}_6\text{H}_5$		Found.			
		I.	II.	III.	IV.
S	12.97	13.04	13.1
N	5.68	5.62	5.56

Like sulphonanilides in general, this substance is very readily soluble in dilute alkalis, differing markedly in this respect from its analogue orthotolanilide, $\text{CH}_3\text{C}_6\text{H}_4\text{CONH.C}_6\text{H}_5$, with which it was compared. Its solution in alkalis is much more stable than that of orthotolanilide. When the alkaline solution of the latter is boiled, the odor of aniline is at once perceptible in the passing steam. The alkaline solution of the sulphonanilide can be boiled for some time before aniline can be detected in the steam, and it requires protracted boiling to decompose a few grams of it completely. This difference between the two classes of anilides is even more marked when they are boiled with dilute acids. Orthotolanilide can be almost completely saponified by boiling with hydrochloric acid (1 to 10). Acid of this dilution has practically no effect upon the sulphonanilide. Five grams of the latter were boiled with 500 cc. of such a mixture for ten hours. On cooling, somewhat more than 4 grams of the unchanged anilide crystallized out; the difference approximately represents the solubility of the sulphonanilide in water. As mentioned in another connection, these facts seem to justify the conclusion that the comparative ease with which one of the aniline residues, in orthosulphobenzanilide, can be removed without disturbing the other, is due to the fact that the former is connected with carbon and the latter with sulphur.

Orthosulphanilidobenzoic Acid.—This substance was obtained by oxidizing orthotoluenesulphonanilide with potassium permanganate in an alkaline solution. The oxidation could not

be made to give anything like a quantitative yield. An attempt was first made to oxidize the sulphonanilide by suspending it, in a finely divided condition, in a considerable quantity of hot water and then adding a solution of potassium permanganate. By this method very little of the anilic acid was obtained, as, in consequence of the insolubility of the anilide and the solubility of the anilic acid, the latter was further broken down, almost as rapidly as it was formed. The best results were obtained by working with small quantities of the anilide in a solution of caustic potash. 5 grams of ortho-toluenesulphonanilide were dissolved in a liter of water containing 2 grams of caustic potash, and the solution heated in a bath of boiling water. When the solution had reached the temperature of the bath, permanganate was added, in 5 gram portions, until 20 grams had been added.

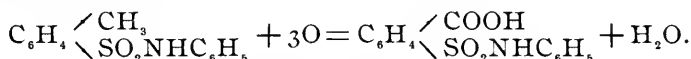
This amount of permanganate was not sufficient to oxidize all the anilide used, but the addition of more seemed to affect the product fully as much as the anilide, while by working with the amounts given, the unoxidized anilide could readily be recovered and used in subsequent oxidations. When the color of the permanganate had entirely disappeared, the oxides of manganese were removed by filtering the hot liquid through cloth and paper, and the filtrate was carefully neutralized with hydrochloric acid. The neutralization, at this stage, is rendered necessary by the fact that the anilic acid undergoes considerable decomposition when its alkaline solution is concentrated by evaporation. The neutral solution was then evaporated to a small volume and acidified with concentrated hydrochloric acid. This precipitated both the unchanged anilide and the anilic acid formed. The precipitate was filtered off, thoroughly washed with cold water, and then boiled with an excess of barium carbonate suspended in a liter of water. The solution, containing the barium salt and small quantities of unchanged anilide, was evaporated to dryness, powdered, and repeatedly extracted with small quantities of absolute alcohol to remove the last traces of unoxidized anilide. The barium salt was then crystallized from water and the acid liberated by acidifying with hydrochloric acid. One crystallization from

water of the acid prepared in this way gave a perfectly pure product which melted sharply at 156°.

Orthosulphanilidobenzoic acid is readily soluble in hot water, difficultly soluble in cold water, alcohol, and ether. The analyses of the barium and aniline salts show that its composition is $C_{13}H_{11}O_4N_3S$, and the method of preparation leads to the structure represented by the formula



it being formed according to the equation



Salts of Orthosulphanilidobenzoic Acid.—The salts which orthosulphanilidobenzoic acid forms with the alkalies are all extremely soluble in water and no effort was made to obtain them in pure condition. The barium salt, prepared as mentioned above, crystallizes in small, colorless needles, which usually form in star-like groups and have no well-developed crystal-planes. An analysis gave the following results:

0.2001 gram substance gave 0.0674 gram $BaSO_4$.

0.2251 gram substance gave 0.0763 gram $BaSO_4$.

Calculated for $(C_6H_4 \begin{array}{l} \diagup CO.O \\ \diagdown SO_2NHC_6H_5 \end{array})_2 Ba.$		Found.	
		I.	II.
Ba	19.98	19.8	19.91

Summary.

Briefly stated, the results obtained in this investigation are as follows:

I. The product of the action of phosphorus pentachloride upon salts of orthosulphobenzoic acid is a mixture of two chlorides, one a solid, the other apparently an uncrystallizable oil.

II. The solid chloride is the symmetrical dichloride of orthosulphobenzoic acid represented by the formula $C_6H_4 \begin{array}{l} \diagup COCl \\ \diagdown SO_2Cl \end{array}$.

III. The product of the action of aniline upon the dry, solid chloride is symmetrical orthosulphobenzanil, which has the structure represented by the formula $C_6H_4 \begin{array}{l} \diagup CO \\ \diagdown SO_2 \end{array} NC_6H_5$.

IV. The product of the action of aniline upon the solid chloride in an emulsion of water is symmetrical orthosulphobenzanilide, which has the structure represented by the formula $C_6H_4 \begin{matrix} / CONHC_6H_5 \\ \backslash SO_2NHC_6H_5 \end{matrix}$.

V. The product of the action of aniline upon the liquid chloride of orthosulphobenzoic acid is the infusible anilide.

III.—SEPARATION OF THE TWO CHLORIDES OF ORTHO-SULPHOBENZOIC ACID.

BY IRA REMSEN AND A. P. SAUNDERS.

Although the attempts made by Remsen and Kohler to separate the two chlorides of orthosulphobenzoic acid were not successful it was now decided to undertake further experiments with this object in view. Additional solvents were employed and the crystallizations were carried on at lower temperatures. It so happened that the winter during which this work was done was exceptionally cold and therefore especially favorable for the crystallization. The success of the experiments is in part at least to be ascribed to this fact.

The chlorides are easily soluble in ether and chloroform as stated by Remsen and Kohler, but it has not proved possible to separate them by crystallization from these solvents. They are also very soluble in benzene, toluene, xylene, turpentine, acetone, carbon bisulphide, and glacial acetic acid, but from these solutions only oils are obtained or oily masses containing crystals.

I. *Crystallization of the Chlorides from Petroleum Ether.*

In petroleum ether (boiling-point 80°) the chlorides are very sparingly soluble in the cold, but more readily when the solvent is warmed. The solution of the mixed chlorides in hot petroleum ether, if nearly saturated, becomes milky on cooling, and an oil settles to the bottom. If the vessel be placed in a freezing mixture, the oily mass solidifies, and below a certain temperature the separation of crystals begins. These form a layer at the bottom of the vessel and around the sides, consisting of fine needles of the lower-melting chloride,

associated with the broader, square crystals of the solid. From such a mass, it is impossible to make anything like a satisfactory separation, especially because the needles of the lower-melting chloride melt at once if the hand is brought in contact with the vessel, and in melting, dissolve a considerable portion of the other chloride. It is better in using this method to warm the solution to a point not above 30° , and then to pour off from the chlorides in excess; in this way very little oil separates from the solution before the temperature is reduced to such a point that crystallization begins. But owing to the slight solubility of the chlorides in petroleum ether, only a small quantity is deposited from solution between 10° – 15° , where crystallization begins, and 0° or -10° , the temperature to which the solution is cooled; furthermore, when the vessel is plunged into a freezing-mixture and quickly cooled, the crystals that separate are very minute and not well formed. Hence the best method of obtaining pure crystals is to cool down to about 0° , and then cause evaporation to take place; the most favorable conditions are those in which the solution can be placed out of doors and allowed to stand over night or for a couple of days; if the temperature remain at 0° or below, fine crystals are obtained.

The higher-melting chloride forms square, hollow crystals, similar in shape to those produced by recrystallization from ether, only the latter are better formed and not hollow. The melting-point is 76° – 77° uncorr. The lower-melting chloride forms radiating clusters of delicate, glistening white needles, sometimes as much as three to four centimeters in length. The melting-point of these crystals is 21.5° – 22.5° uncorr.

The conditions of the open air can be imitated by keeping the beakers used for crystallization in running water or in a freezing mixture and drawing air over the surface of the liquid; in this way good crystals of both chlorides can be obtained.

Although the lower-melting chloride generally begins to form crystals at about 10° when separating from solution, it has been found advisable in all crystallizations to add a nucleus of a few crystals, or a small fragment of the mixed chlorides in the solid form, as soon as the solvent has cooled

down to 10° – 15° , a point at which there is no danger that the nucleus itself will be melted. Several recrystallizations were found necessary in order to obtain either one of the chlorides quite pure.

It will be seen that the above method is tedious to carry out and gives only a small yield of pure products in the end, so that where large quantities are desired there is, as yet, no means of obtaining the lower-melting chloride in pure condition, though the higher-melting chloride can be readily obtained pure by the following method, devised by Mr. J. E. Bucher, in this laboratory:

To a convenient quantity of chlorides dissolved in chloroform, concentrated aqueous ammonia is added, and the solutions shaken together for about a minute; the chloroform solution is then drawn off, and, on evaporation, yields pure solid chloride;¹ the liquid chloride is converted by ammonia into a substance soluble in water, whereas, the solid chloride is much less readily attacked.

At the time when the experiments recorded in the following pages were carried out this method was not known, and there was no test for the purity of the samples of the liquid chloride used excepting (1) the melting-point, which does not suffer much change from the presence of even a considerable percentage of solid chloride, and (2) the number of recrystallizations to which the chloride had been subjected; it should, therefore, be stated that while the solid chloride used in the experiments was almost or quite pure, the liquid chloride contained, as a rule, some of the solid; the reactions generally indicate this, but the results are rarely ambiguous.

It seemed likely that there might be some difference in the solubility of the two chlorides in petroleum ether, and that a separation might be effected by treatment with successive portions of the solvent. A quantity of the mixed chlorides was, therefore, treated with six successive washings of warm petroleum ether, and these were then left to stand in a cool room and evaporate spontaneously; from each of the six solutions both chlorides were obtained, and it did not appear that any separation could be brought about by this means.

¹ The names solid chloride and liquid chloride will be used for the present, although both substances are solid at low temperatures.

In these crystallizations a separation of light flakes of white needles insoluble in petroleum ether was frequently observed, and the same substance sometimes appears in the chlorides when they are allowed to stand for some time. These needles were found to be soluble in hot water, separating again as the solution cools; they then melt at 137° , and are undoubtedly orthochlorbenzoic acid, since Remsen and Kohler found that orthochlorbenzoyl chloride is produced either by the action of phosphorus pentachloride on the chlorides of orthosulphobenzoic acid at temperatures above 100° , or by merely heating the chlorides themselves to a somewhat higher point. A certain amount of decomposition goes on during the process of crystallization from petroleum ether by which orthosulphobenzoic acid is obtained; the darkening of color which takes place in solutions which are left exposed is probably due to the charring of particles of dust which find their way in from the air.

Analyses of the Chlorides.—Portions of both chlorides were decomposed in beakers by warming with concentrated nitric acid to which a solution of silver nitrate had been added.

I. 0.2981 gram solid chloride gave 0.3578 gram AgCl.

	Calculated for $C_7H_4SO_3Cl_2$.	Found.
Cl	29.65	29.68

This agrees with the results of Remsen and Kohler, who found in two analyses 29.46 and 29.4 per cent. of chlorine.

I. 0.1112 gram liquid chloride gave 0.1333 gram AgCl.

II. 0.2546 gram liquid chloride gave 0.3109 gram AgCl.

	Calculated for $C_7H_4SO_3Cl_2$.	Found.	
		I.	II.
Cl	29.65	29.64	30.19

II. *Action of Water on the Chlorides.*

Action in the Cold.—In the cold, water acts with extreme slowness on both of the chlorides.

Two grams of each chloride were placed in 100 cc. of water in a small flask; decomposition began at once, as was shown by testing the water with silver nitrate, but was not complete until about three months had elapsed. The solutions were left to stand over summer, and were then treated with silver carbonate in the hope that, as they had not been heated, it might be possible to obtain two kinds of silver salts; but on

allowing the solutions to evaporate spontaneously, similar crystals were obtained from each, and there was no indication of the formation of two substances.

Action on Heating.—In hot water the chlorides are not rapidly decomposed, but, on boiling, reaction soon sets in, and decomposition is complete after five to ten minutes when small quantities are used; neither in this reaction, nor where the decomposition went on in the cold, was any characteristic difference noted in the rate of reaction for the two substances. From the acids obtained by boiling the chlorides separately with water, barium salts were obtained identical in appearance, behavior, and in composition, as the analyses show.

0.1021 gram neutral barium salt from the acid obtained by decomposition of the solid chloride gave 0.0631 gram BaSO_4 .

	Calculated for $\text{C}_7\text{H}_4\text{SO}_5\text{Ba} + 2\text{H}_2\text{O}$.	Found.
Ba	36.73	36.35

0.1278 gram neutral barium salt from the acid obtained by decomposition of the liquid chloride gave 0.0807 gram BaSO_4 .

	Calculated for $\text{C}_7\text{H}_4\text{SO}_5\text{Ba} + 2\text{H}_2\text{O}$.	Found.
Ba	36.73	37.14

III. *Action of Ammonia on the Chlorides.*

Aqueous Ammonia.—Both chlorides, when heated with dilute ammonia, gave solutions which had an intensely sweet taste, and from which, on acidifying, crystals identical in appearance and having the characteristic taste of benzoic sulphinide were obtained. Mr. A. D. Chambers, working in this laboratory, has recently studied the action of concentrated ammonia on the chlorides in the cold, and finds that two substances are formed; the one from the liquid chloride is probably the ammonium salt of an acid having the formula,



Dry Ammonia Gas.—The following experiments are of interest as showing that the above substance is only obtained from the liquid chloride.

1. Dry ammonia gas was passed into an ether solution of 0.5 gram of the solid chloride. A white precipitate was

formed in the ether, probably ammonium chloride. When the ether was allowed to evaporate, a crystalline residue, which had an intensely sweet taste was obtained. When treated with water, this all went into solution, and on the addition of hydrochloric acid, saccharine separated.

2. Dry ammonia gas was passed into an ether solution of 0.7 gram liquid chloride; a white precipitate separated as above. On evaporation, a crystalline mass was obtained which tasted slightly of saccharine; this went into solution readily in water; on addition of hydrochloric acid, no crystals were obtained, but on warming over the water-bath, a few crystals of saccharine separated.

These solutions were then left to stand and were not again studied until after the experiments of Mr. Chambers, mentioned above. When both solutions had completely evaporated, that from the solid chloride gave a mixture containing ammonium chloride and saccharine as a white crystalline mass, whereas that from the liquid chloride gave ammonium chloride and radiating compact masses of brownish needles, very soluble in water, having a bitter taste, and melting at about 115° . They are very soluble also in alcohol, and from that solvent are obtained as white botryoidal masses of minute needles melting at 116° – 120° . The yield, after recrystallization, was 0.45 gram. These crystals are evidently identical with those discovered by Mr. Chambers, and are apparently not produced at all from the solid chloride; on the other hand, the formation of a slight quantity of saccharine from the liquid chloride may have been due either to the presence in it of some of the solid chloride, or to a transformation of the compound $C_6H_4 \begin{smallmatrix} \diagup CN \\ \diagdown SO_2.OH \end{smallmatrix}$ into saccharine.

IV.—*Action of Phenol on the Chlorides.*

Action on The Mixed Chlorides.—When the mixed chlorides are added to phenol they pass into solution, but in the cold no reaction takes place. On warming, however, the evolution of hydrochloric acid begins at once, and the liquid assumes a clear lake-red color, which becomes more and more intense as the reaction proceeds. If the reaction is allowed to go on quietly to the end, with occasional momentary heating over

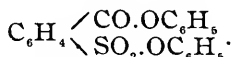
the flame, a viscous, opaque red mass is obtained, which becomes thick and gummy when cold. If it is poured, while hot, into a solution of sodium hydroxide, it at once takes on the characteristic color of phenolphthalein—an intense purple; at the same time a portion separates as an insoluble crystalline cake and can, by filtration and washing with water, be obtained quite free from the colored substance. This crystalline substance is readily soluble in hot alcohol, sparingly in cold, insoluble in water, and crystallizes from alcohol in shining leaflets or slender flat needles which melt at 117.5° – 118.5° uncorrected.

When boiled with a concentrated solution of potassium hydroxide it melts and is ultimately decomposed, for, on acidifying, the odor of phenol is plainly perceived, and when bromine water is added a considerable deposit of tribromphenol is formed. The substance gave, on analysis, the following results :

- I. 0.1753 gram gave 0.4156 gram CO_2 and 0.0754 gram H_2O .
- II. 0.0917 gram gave 0.2150 gram CO_2 and 0.0381 gram H_2O .
- III. 0.1579 gram gave 0.3731 gram CO_2 and 0.0645 gram H_2O .
- IV. 0.1696 gram gave 0.3974 gram CO_2 and 0.0670 gram H_2O .
- V. 0.1934 gram gave 0.1309 gram BaSO_4 .
- VI. 0.1820 gram gave 0.1194 gram BaSO_4 .

	Calculated for $\text{C}_{19}\text{H}_{14}\text{SO}_5$.	I.	II.	III.	Found. IV.	V.	VI.
C	64.41	64.65	63.95	64.44	63.91
H	3.95	4.78	4.61	4.54	4.39
S	9.04	9.34	9.02

From the analytical results, the method of formation, and the chemical behavior of this compound, it appears that it is the diphenyl ether of orthosulphobenzoic acid, of the formula



The combustions of this substance and of all others analyzed were made by the lead chromate method, as described by De

Roode.¹ The sulphur determinations were made by the Liebig method, excepting in two cases where it was found necessary to use that of Carius.

Action on the Solid Chloride.—When the pure solid chloride is heated with phenol, hydrochloric acid is given off. If the reaction is checked after a few moments, the product is almost entirely the phenol ether above described, though there is also formed at the same time some of the colored substance.

1 gram of pure chloride gave in this way 0.6 gram of phenol ether. If, however, the boiling is continued for some time longer, the reaction seems to enter on a second stage, with the formation of a larger quantity of the colored product. 2.3 grams heated for ten minutes gave only 0.5 gram of phenol ether and more than 1 gram of the red compound.

Action on the Impure Liquid Chloride.—A small quantity of the liquid chloride, containing also some of the solid, was heated for a short time with phenol. The usual color was obtained, though it was not very intense, and on pouring the liquid into dilute alkali, a heavy yellow oil settled to the bottom; this became crystalline after some time, and on recrystallization from alcohol yielded two products; one in leaflets identical in appearance with the phenol ether; the other in clear thin columns melting at 98° – 100° uncorrected.

V.—*Action of Benzene and Aluminum Chloride on the Chlorides.*

The benzene used in these experiments was dried over sodium. The aluminium chloride was, for the most part, the commercial resublimed product; it was always used in these reactions in about the proportions given below (page 362).

When aluminium chloride is added to a solution of the mixed chlorides in benzene, reaction begins at once. At first, bubbles of hydrochloric acid are given off slowly, but after a few moments the solution becomes warmer and reaction sets in vigorously; by plunging the vessel in cold water the evolution of hydrochloric acid is much retarded, but on warming again, even in the hand, it at once resumes its former activity. It has proved possible by controlling this reaction to get different products.

¹ This Journal, 12, 226.

I.—*Action on the Mixed Chlorides in the Cold.*—On leaving the vessel in which the reaction goes on, in cold water, hydrochloric acid is given off gently for twenty minutes or half an hour. There then remains an almost or quite opaque red solution, with sometimes a heavy opaque layer separated at the bottom. If this liquid is now poured into a small quantity of dilute hydrochloric acid cooled, or containing pieces of ice, and stirred vigorously for a few moments, the color disappears, the water becomes cloudy, and a layer of almost colorless benzene floats on the top; this is poured off and quickly evaporated. When the benzene is all driven off there remains a clear viscous oil, which if left to stand, crystallizes after some time forming a solid dry cake; solidification can be quickly induced by rubbing with a rod. Care must be taken not to heat longer than is necessary in driving off the benzene, as decomposition is apt to take place. The crystalline mass obtained is insoluble in water, but dissolves readily in ether if powdered and shaken with that solvent; from this solution, by spontaneous evaporation, fine crystals are obtained with very well-developed faces. Their melting-point is 96° – 97° uncorrected. This substance is soluble in alcohol, ether, and benzene, sparingly in petroleum ether. It appears to be a compound in which one of the chlorine atoms of orthosulphobenzoyl chloride has been replaced by a phenyl group.

I. 0.2322 gram gave 0.1183 gram AgCl.

II. 0.1367 gram gave 0.0695 gram AgCl.

III. 0.1775 gram gave 0.1470 gram BaSO₄.

IV. 0.1363 gram gave 0.1137 gram BaSO₄.

	Calculated for C ₁₃ H ₉ SO ₃ Cl.	I.	II.	Found.	III.	IV.
Cl	12.66	12.60	12.58
S	11.41	11.39	11.46

There are several possible formulas for a substance of this composition, but its reactions and decompositions show that it is in all probability derived from the symmetrical chloride of orthosulphobenzoic acid by the substitution of phenyl for the chlorine atom connected with carbon, as represented by the formula, $\text{C}_6\text{H}_5\text{C}(\text{SO}_2\text{Cl})\text{CO}\cdot\text{C}_6\text{H}_5$. In accordance with this view

the name orthobenzoylbenzenesulphone chloride is given to the substance.

According to the theory of the structure of the two chlorides of orthosulphobenzoic acid it is to be expected that two different substances might be produced in the reaction with benzene and aluminium chloride in the cold. All efforts to obtain a second product from this reaction have so far been unsuccessful. When the product is recrystallized from ether there is always a certain amount of a heavy oily substance produced, but this appears to be the acid, identical with that obtained when pure orthobenzoylbenzenesulphone chloride is boiled with water.

The reaction with benzene and aluminium chloride is always accompanied by the formation of colored products. If the vessel in which the reaction has been performed is allowed to stand for a day, the residues turn a fine violet or green color.

Orthobenzoylbenzenesulphone Chloride, when left exposed to the air, absorbs water and decomposes, yielding a thick liquid not unlike the aqueous solution of orthosulphobenzoic acid. If allowed to stand in cold water the chloride is not immediately attacked, but if boiled for about ten minutes decomposition is complete. In this way an acid solution is obtained which at first gives no crystals even when evaporated until it is syrupy; but, if then allowed to stand for some time, long transparent crystals are formed. According to the above view this acid has the structure represented by the formula



Potassium Orthobenzoylbenzenesulphonate.—The acid solution above mentioned, when neutralized with potassium hydroxide, gives a very soluble potassium salt which crystallizes well from concentrated aqueous solution, but better from alcohol, in which it is somewhat less soluble. The crystals thus obtained are very well formed, with perfect faces. When crystallized either from water or from 95-per cent. alcohol the substance, when quickly heated, melts at 122° – 124° , but if it is slowly heated the melting-point rises to about 175° .

I. 0.4569 gram of the crystals obtained from water, when heated for eight hours at about 115° , lost 0.0264 gram. The calculated loss for one molecule of water from the compound $\text{C}_{13}\text{H}_9\text{SO}_4\text{K} + \text{H}_2\text{O}$ is 0.0275 gram.

II. 0.7479 gram of the crystals obtained from alcohol, heated in the same way lost 0.0427 gram. The calculated loss is 0.0423 gram.

The melting-point of the dried salt is 181.5° – 182.5° uncorr.

On analysis the following results were obtained for the hydrated salt :

I. 0.1742 gram gave 0.1327 gram BaSO_4 .

II. 0.1630 gram gave 0.1233 gram BaSO_4 .

III. 0.1597 gram gave 0.1172 gram BaSO_4 .

IV. 0.2145 gram gave 0.0582 gram K_2SO_4 .

V. 0.1702 gram gave 0.0461 gram K_2SO_4 .

Calculated for $\text{C}_{13}\text{H}_9\text{SO}_4\text{K}+\text{H}_2\text{O}$.		I.	II.	Found. III.	IV.	V.
S	10.06	10.47	10.40	10.09
K	12.26	12.16	12.15

From the anhydrous salt the following result was obtained :
0.1973 gram gave 0.1556 gram BaSO_4 .

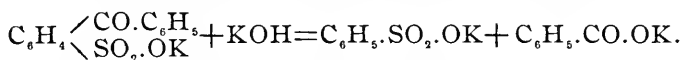
Calculated for $\text{C}_{13}\text{H}_9\text{SO}_4\text{K}$.		Found.
S	10.67	10.85

This potassium salt can be more easily obtained by allowing the chloride itself to react directly with caustic potash, with application of a very little heat ; in this way a solid mass of the salt is at once obtained.

If the salt is further heated with dry potassium hydroxide, it decomposes almost quantitatively, yielding benzoic acid and benzenesulphonic acid. When the products of decomposition are dissolved in water, and this solution acidified the benzoic acid is precipitated in small white crystals which, when separated on the filter, washed, and dried, melt at 120° . They dissolve in hot water and give the characteristic odor of benzoic acid ; they sublime, forming the well-known delicate laminæ, and giving at the same time the usual odor. The filtrate, when evaporated to dryness, yields a mixture of potassium chloride and a more soluble salt. On treatment with phosphorus pentachloride an oil is obtained having the peculiar odor of benzenesulphone chloride, and this oil, when treated with ammonia, gives an amide sparingly soluble in water in the cold, more readily on warming, and melting

at 145° – 147° . The melting-point of benzenesulphone amide when pure, is 149° .

This decomposition of potassium orthobenzoylbenzenesulphonate is therefore to be represented by the equation



Ethyl Ether of Orthobenzoylbenzenesulphonic Acid.—The chloride of this acid, as mentioned above, is soluble in alcohol and crystallizes from that solvent; but when a recrystallization was attempted a new product was obtained, having the melting-point 125.5° – 126.5° uncorr. On attempting to prepare a quantity of this substance no satisfactory results were obtained. Several grams of the chloride, when heated with absolute alcohol on the water-bath for a day, yielded on evaporation only free acid; furthermore, the ethyl ether itself on recrystallization from alcohol gradually decomposes, giving the free acid again. This is in accordance with the recent work of Krafft and Roos,¹ who found that benzenesulphone chloride was transformed into the acid by treatment with alcohol. The ethyl ether was obtained on crystallizing the chloride from a mixture of ether and alcohol by allowing the solution to stand for a few days. This tendency to pass over into the acid may account for the very high figures obtained for hydrogen in combustion.

The analysis of the compound yielded the following results:

I. 0.1233 gram gave 0.2827 gram CO_2 and 0.0640 gram H_2O .

II. 0.1192 gram gave 0.2736 gram CO_2 and 0.0647 gram H_2O .

III. 0.1781 gram gave 0.1409 gram BaSO_4 .

IV. 0.1739 gram gave 0.1392 gram BaSO_4 .

	Calculated for $\text{C}_{15}\text{H}_{14}\text{SO}_4$.	I.	II.	Found.	III.	IV.
C	62.07	62.53	62.60
H	4.83	5.78	6.04
S	11.03	10.88	11.01

Lactim of Orthobenzoylbenzenesulphonic Acid.—It was at first supposed that the action of ammonia on the chloride of this

¹ Ber. d. chem. Ges., 26, 2827.

acid would furnish an amide of the formula $C_6H_4 \begin{smallmatrix} \diagup CO.C_6H_5 \\ \diagdown SO_2.NH_2 \end{smallmatrix}$ and in order to obtain this compound some of the chloride in ethereal solution was subjected to the action of dry ammonia gas. A separation of ammonium chloride occurred at once, and after a few minutes the reaction was complete. The ethereal solution was filtered off and evaporated to dryness. The product thus obtained is a crystalline substance insoluble in water, sparingly soluble in cold alcohol, more readily in hot, and crystallizing from that solvent in flat leaf-like plates which are quite white, and melt at 163° uncorr. The results of the analyses are given below:

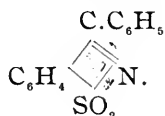
- I. 0.1454 gram gave 0.3437 gram CO_2 and 0.0555 gram H_2O .
- II. 0.0928 gram gave 0.0914 gram $BaSO_4$.
- III. 0.1362 gram gave 0.1362 gram $BaSO_4$.
- IV. 0.2065 gram gave 10.01 cc. nitrogen.¹

	Calculated for $C_{13}H_9SO_2N$.	I.	II.	Found. III.	IV.
C	64.20	64.47
H	3.70	4.24
S	13.17	...	13.54	13.75	...
N	5.76	6.01

That the substance is not the amide is plainly shown by the above results; the values calculated for the amide of the formula given are:

$$C = 59.77; H = 4.21; S = 12.26; N = 5.36.$$

The formation of a lactin in this way accords with the general behavior of such aromatic amides of the ortho series; the formula of the compound thus produced by loss of water from the amide is in all probability,



Anilide of Orthobenzoylbenzenesulphonic Acid.—When the chloride of the acid is heated for a few minutes with aniline and then poured into moderately concentrated hydrochloric acid, a gummy mass is obtained which, when the aniline is

¹ The estimation of nitrogen was kindly made for us by Mr. G. W. Gray, of this laboratory, using the absolute method.

all dissolved out, becomes solid and crystalline. By filtering and washing, the crystalline product is obtained fairly pure. It is moderately soluble in hot alcohol, sparingly in cold, and crystallizes in flat narrow blades or needles which melt at 143° – 145° uncorr. At the same time short square crystals are formed which have the same melting-point, and are probably only another form of the same substance. An analysis of the needles gave the following results:

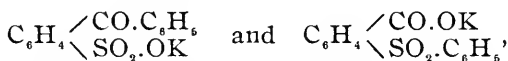
0.0924 gram gave 0.0669 gram BaSO_4 .

	Calculated for $\text{C}_{19}\text{H}_{16}\text{SO}_3\text{N}$.	Found.
S	9.56	9.95

Structure of the Compounds described above.—The structure of these compounds is clearly shown by the following considerations:

1. The very easy solubility of the acid obtained by the decomposition of the chloride with water. Such sulphonic acids are in general readily soluble, whereas the analogous carboxylic acids are sparingly soluble.

2. The decomposition of the potassium salt on fusion with potassium hydroxide by which benzoic acid and benzenesulphonic acid result. It is possible to imagine the formation of these products from either of the substances



but diphenylsulphone itself, when fused with potassium hydroxide, breaks down in a complicated way, giving several different products, including phenol, diphenyl, and sulphur dioxide. Furthermore, the reaction is not very readily brought about, whereas in the above case the decomposition is perfectly smooth and clean. It will also be shown later that a substance having the probable formula $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CO} \cdot \text{C}_6\text{H}_5 \\ \diagdown \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{array}$ breaks down under similar circumstances, giving benzoic acid and diphenylsulphone.

3. The fact that the ethyl ether suffers gradual decomposition in the presence of alcohol, giving the free acid again, accords much better with the supposition that the acid is a sulphonic acid than that it is a carboxylic acid.

4. The formation of a lactim is also an argument in favor of the presence of the ketone group.

2. *Action of Benzene and Aluminium Chloride on Orthobenzoylbenzenesulphone Chloride.*—2 grams of the chloride were dissolved in benzene and about 3 grams of aluminium chloride added. The reaction was scarcely perceptible when the heat of the hand only was applied, but after warming a moment in the flame the reaction went on briskly. At the end the solution was poured into water as usual. In this way a certain amount of tarry material was obtained, but the benzene solution, on evaporation, gave a mass of crystals which, when recrystallized from alcohol, melted at 183° – 185° , and had the appearance of a compound of the same melting-point which will be described below, and which is obtained as the end-product of the action of benzene and aluminium chloride on the solid chloride of orthosulphobenzoic acid. The yield corresponded to about 55 per cent. of that calculated.

This shows orthobenzoylbenzenesulphone chloride to be an intermediate product of the action of benzene and aluminium chloride on one of the chlorides of orthosulphobenzoic acid, probably the solid, as will appear.

3. *Action on the Pure Solid Chloride of Orthosulphobenzoic Acid.*—The reaction in the case of all these chlorides is singularly variable; slight differences of temperature appear to cause serious variations in the results obtained, and probably the purity of the materials is also an important factor.

The pure solid chloride does not enter into reaction as readily as the mixed chlorides. It does, however, react slowly when warmed in the hand, and this reaction when carried out as previously directed gives rise to the formation of orthobenzoylbenzenesulphone chloride, though the yield is not large, as some of the material goes over into a gummy mass from which nothing definite was obtained, and in some cases nothing but gummy material was produced.

2 grams of pure solid chloride gave about 1 gram of orthobenzoylbenzenesulphone chloride.

4. *Action on the Mixed Chlorides when Heated.*—This reaction, which was the first one used, was studied for a long time and under a variety of conditions in the hope that two distinct

products might be obtained from it, but, although the crystalline product mentioned as being obtained by the action of orthobenzoylbenzenesulphone chloride was invariably produced, it has never proved possible to obtain a corresponding product from the liquid chloride, though, as will be shown later, there are indications that an isomeric product was obtained when the latter chloride in very pure condition, was used.

The reaction with the mixed chlorides goes on best in this way: 10–20 grams of chloride are dissolved in four or five times that weight of benzene in a large test-tube or a beaker, and to the solution, aluminium chloride is added in two or three quantities until the weight is about equal to that of the chloride used. Heat is then applied to the vessel from time to time, by which the reaction is accelerated. After about twenty minutes it is complete. If the solution is now heated again and removed, the evolution of gas ceases at once; nor does further addition of aluminium chloride cause a renewal of the reaction. The end may be recognized in this way:

The product so obtained is an opaque, or nearly opaque, red liquid, with a heavy layer, almost black, at the bottom. The whole mass is poured into hot water. If any aluminium chloride is present in excess it is violently attacked, and that which has entered into reaction is set free, with evolution of a good deal of heat. By this means the benzene present is almost entirely driven off; the last portions are expelled by further heating. The product thus obtained is a brownish, granular mass, the color of which varies in different instances. It is sometimes pale and semi-crystalline; at others, darker and gummy. By filtering and washing, all the aluminium is got rid of, and the substance may be dried and recrystallized from hot alcohol, in which it is somewhat soluble, though almost insoluble in cold. The product thus obtained is, as a rule, more or less colored, either brown or dull violet, and this color is very difficult to get rid of either by boiling with animal charcoal or by recrystallization. Even the purest samples were still slightly colored. When crystallized slowly from alcohol it forms leaflets of irregular surface, generally terminated by an obtuse angle. These melt at 183.5° – 184° uncorr.

Better crystals are obtained from benzene, in which it is more readily soluble. It is sparingly soluble in ether, and quite insoluble in water; it dissolves in concentrated nitric acid and in concentrated sulphuric acid, and is obtained unchanged from both. Analyses gave the following results:

I. 0.1850 gram gave 0.4792 gram CO_2 and 0.0826 gram H_2O .

II. 0.1692 gram gave 0.4433 gram CO_2 and 0.0738 gram H_2O .

III. 0.1341 gram gave 0.0915 gram BaSO_4 (Carius).

IV. 0.1303 gram gave 0.0984 gram BaSO_4 .

V. 0.1882 gram gave 0.1377 gram BaSO_4 .

	Calculated for $\text{C}_{19}\text{H}_{14}\text{SO}_3$.	I.	II.	Found. III.	IV.	V.
C	70.81	70.65	71.45
H	4.35	4.96	4.84
S	9.94	9.39	10.37	10.06

From the method of preparation it seemed likely that this substance was a diphenyl derivative having the structure represented by the formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \cdot \text{C}_6\text{H}_5 \\ \diagdown \text{SO}_2 \cdot \text{C}_6\text{H}_5 \end{smallmatrix}$. This view is confirmed by the properties and reactions of the compound.

It is stable in the presence of ordinary reagents. As mentioned above, it dissolves undecomposed in strong nitric and sulphuric acids; a mixture of fuming nitric acid and sulphuric acid, heated to boiling, attacks it with the formation of a non-crystalline yellow product, soluble in alcohol. Alcoholic potash has no action even when the substances are boiled together for a day. The compound may be heated alone to 250° without change, but at a somewhat higher temperature it sublimes with slight decomposition; the sublimate consists of the original substance.

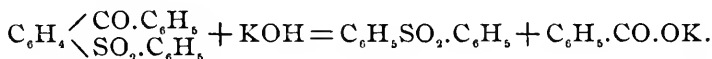
When fused with potassium hydroxide it is decomposed, and this reaction furnishes the strongest evidence in favor of the structural formula given above. If the substance is heated slowly with caustic potash in excess, the reaction takes place rapidly at 200° – 210° , with formation of a yellowish-brown mass. This, when warmed with water, partially dissolves. The residue, separated by filtration and recrystalliza-

tion from alcohol, gives the characteristic rhombic crystals of diphenylsulphone, melting at 123° – 124° and having the solubility and general character of that compound. The filtrate treated with hydrochloric acid gives a precipitate of benzoic acid. The results are nearly quantitative.

The benzoic acid obtained in this way melts at 119° – 120° , is soluble in hot water, giving the usual odor, and separates out in small crystals as the solution cools; it sublimes in thin leaflets, and shows in every way the properties of benzoic acid. The identity of the diphenylsulphone was at first questioned on account of a discrepancy between its melting-point and that given for the substance in Beilstein's *Handbuch*, where the melting-point 128° – 129° is quoted from Otto,¹ who prepared it by the action of benzenesulphone chloride on mercury diphenyl. But in an earlier article,² Otto gives the melting-point of a quantity prepared by the action of benzenesulphone chloride on benzene and aluminium chloride as 124° . Other observers give various other values; as 125° – 126° ,³ 126° ,⁴ 128° .⁵

To determine, if possible, whether the variations were due to differences of purity, about 20 grams of diphenylsulphone were carefully investigated. The substance was prepared by Dr. R. M. Parks, in this laboratory, by the action of benzene and aluminium chloride on benzenesulphone chloride. It was already fairly pure, and melted after one recrystallization at 122.5° – 124° . It was then subjected to six recrystallizations from alcohol and from alcohol and water, and the melting-point taken from time to time. This varied very little, and the substance finally obtained, which had the appearance of a perfectly pure product, melted at 122.5° – 123.5° uncorr.

The decomposition above referred to takes place, no doubt, according to the equation



¹ Ber. d. chem. Ges., 18, 248.

² *Ibid*, 11, 2066.

³ Knapp: Ztschr. Chem., 1869, 41.

⁴ Stenhouse: Ann. Chem. (Liebig), 140, 290.

⁵ Freund: *Ibid*, 120, 81.

In accordance with this view the substance is named orthobenzoyldiphenylsulphone. If it has the above structural formula, it is, in one sense, a ketone, and it was expected that it would yield the usual derivatives with phenylhydrazine and with hydroxylamine. Several attempts were made to bring about the formation of such products, but in vain.

5. *Action on the Pure Solid Chloride when Heated.*—One gram of pure solid chloride, when submitted to reaction and several times warmed, yielded a certain amount of gummy material and 0.7 gram of crystalline product, which, when dissolved in alcohol, deposited 0.4 gram pure orthobenzoyldiphenylsulphone; hence the yield corresponds in this reaction to about 50 per cent. of the calculated quantity, and could no doubt be increased by carefully regulating the conditions. The facts described show clearly that this substance is derived from the solid chloride. It then becomes a matter of great interest to determine, if possible, what becomes of the liquid chloride in the reaction on the mixed chlorides. As mentioned above, no definite product has as yet been obtained from that reaction, corresponding to the liquid chloride. The water in which the benzene is poured after the reaction, has several times been evaporated, but yields little or nothing but inorganic substances.

There is always a quantity of gummy or tarry material formed which is more soluble in alcohol than the benzoyldiphenylsulphone, and this can be washed out with warm alcohol. On evaporation only the original gum is obtained. On sublimation of this, a substance is given off at a high temperature and crystallizes on the sides of the vessel in yellow needles, while, at the same time, an oil is also obtained, which was not further studied. The yellow needles, which melt at 205° – 207° , with previous softening, are somewhat soluble in hot alcohol, sparingly in cold. The solution is yellow by transmitted light, and brilliant blue by reflected light. On recrystallization the yellow color almost entirely disappears, but the blue fluorescence remains, and is apparently due to the compound itself and not to an impurity.

6. *Action on the Liquid Chloride when Heated.*—It was only in the early stages of this investigation that any considerable

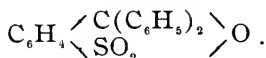
quantity of the liquid chloride in pure condition was available. At that time the purest samples gave very little if any orthobenzoyldiphenylsulphone, but yielded mostly gummy or tarry masses from which very little could be obtained. A few crystals were produced at one time which had a different habit, and melted at 161° – 162° uncorr. Many efforts have since been made to prepare a further quantity of this product, but always without success. That on hand was finally purified as well as possible, with so small a quantity, and submitted to analysis, with the following results:

I. 0.1223 gram gave 0.3122 gram CO_2 and 0.0537 gram H_2O .

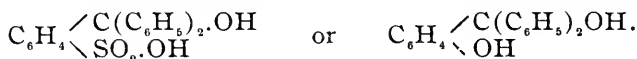
II. 0.0827 gram gave 0.0665 gram BaSO_4 .

	Calculated for $\text{C}_{19}\text{H}_{14}\text{SO}_3$.	I.	Found. II.
C	70.81	69.63
H	4.35	4.88
S	9.94	9.39

These results, though not satisfactory, indicate that the substance is probably an isomer of orthobenzoyldiphenylsulphone, perhaps a substance of the formula



When dropped into fusing caustic potash the compound reacts, giving an intense carmine color. This suggests the possible formation of such a triphenyl-methane derivative as



Summary.

The main results reached in this investigation may be summarized as follows:

1. It has been found possible by the use of petroleum ether to separate two chlorides of orthosulphobenzoic acid in crystalline form; one melts at 21.5° – 22.5° uncorr., the other at 76° – 77° uncorr. The latter was already known in crystalline form, and the existence of a second chloride had been indicated by the reactions of the mixed chlorides. Both of these chlorides, when heated with water, give orthosulphobenzoic acid; and the same results have always thus far been obtained

when they are allowed to decompose in the presence of water in the cold.

2. When treated with ammonia, the pure solid chloride gave saccharine and ammonium chloride, and no other product could be detected; the liquid chloride, on the other hand, gave saccharine in part, but also a large yield of a second product which is probably the ammonium salt of orthocyanbenzenesulphonic acid.

3. When treated with phenol, both chlorides apparently have a tendency to go over finally to a colored substance like phenolphthalein, but yield crystalline products if the reaction is checked after a few moments. In this way, from the mixed chlorides, and from the pure solid chloride, the normal phenyl ether of orthosulphobenzoic acid is obtained, having the formula $C_6H_4 \begin{smallmatrix} \diagup CO.OC_6H_5 \\ \diagdown SO_2.OC_6H_5 \end{smallmatrix}$.

4. By the action of the mixed chlorides on benzene and aluminium chloride a product is first formed which is, apparently, orthobenzoylbenzenesulphone chloride, $C_6H_4 \begin{smallmatrix} \diagup CO.C_6H_5 \\ \diagdown SO_2.Cl \end{smallmatrix}$.

This decomposes with water, giving a very soluble acid, which yields characteristic salts.

The same compound is obtained when the pure solid chloride is used, whence it appears probable that in its formation from the mixed chlorides it comes from the solid and not from the liquid.

5. By continued action of benzene and aluminium chloride on the chlorides or on this intermediate product, orthobenzoyldiphenylsulphone, $C_6H_4 \begin{smallmatrix} \diagup CO.C_6H_5 \\ \diagdown SO_2.C_6H_5 \end{smallmatrix}$, is obtained.

The same product is also formed when the pure solid chloride is used in the reaction and the substances heated together.

Hence from the solid chloride it is possible to pass at once to orthobenzoyldiphenylsulphone; or the intermediate product, orthobenzoylbenzenesulphone chloride, may be formed, and this, by further action, may be transformed into orthobenzoyldiphenylsulphone.

These reactions all speak in favor of the symmetrical for-

mula $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \cdot \text{Cl} \\ \diagdown \text{SO}_2 \cdot \text{Cl} \end{smallmatrix}$ for the solid chloride of orthosulphobenzoic acid.

In favor of the formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CCl}_2 \\ \diagdown \text{SO}_2 \end{smallmatrix} \text{O}$ for the liquid chloride there is, as yet, little direct evidence. Nevertheless, its action with ammonia and the formation, though in small quantity, of the product described in the text, by reaction with benzene and aluminium chloride, are worthy of attention.

Contributions from the Chemical Laboratory of Purdue University.

XIV. THE SUGAR OF THE *AGAVE AMERICANA*.

BY W. F. STONE AND D. LOTZ.

Under the title of "Researches on the Sugar of the *Agave Americana*," Messrs. Gustave Michaud and José Fidel Tristan have published in this Journal, **14**, 548, a paper which the authors summarize as follows: "The *Agave Americana* contains a sugar of the formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. This sugar differs from all others of the same group except synanthrose, by its inactivity. It differs from synanthrose by its power of crystallizing, by its action on Fehling's solution and by the rotatory power of the products of its inversion. We propose for the sugar the name of *Agavose*."

An inspection of the data presented by the authors, suggested to one of us that, with one exception (the optical inactivity), the properties of agavose were strikingly like those of sucrose under the same conditions. For instance, the authors state that the juice obtained by pressing the leaves of the agave, after treatment with alcohol, basic acetate of lead, and hydrogen sulphide, reduced Fehling's solution about five-eighths as strongly as glucose. This result is however not different from that obtainable from any plant juice which contains sucrose mixed with invert sugar.

Again, after crystals of the sugar had been obtained, they were inverted by heating with 10-per cent. hydrochloric acid at the boiling-point for some time, and the specific rotation was observed to be $(\alpha)_D = -14.39^\circ$ to 14.53° . But these are numbers which might easily result from the inversion of pure sucrose under the given conditions since, as is well known,

levulose is rapidly destroyed by hydrochloric acid at 100° , and the rotatory power of invert sugar correspondingly lowered, so that the accepted method for inversion of sucrose employs very dilute acid and a temperature of 65° .

In watery solution the agavose dissolved calcium oxide which was again precipitated by alcohol or by a current of carbon dioxide. This is also a property of sucrose.

But while the characteristics of agavose thus far described might be explained on the assumption that the juices of the agave contained a mixture of invert and cane-sugar, the optical inactivity of the agavose is not to be accounted for on any such grounds. A new sugar of so abundant occurrence as that of the agave and with the properties described, would be an important and interesting addition to the list of carbohydrates. An opportunity was therefore sought to secure a specimen of agavose in order to verify the properties ascribed to it by Michaud and Tristan as well as to study it farther.

We have obtained two specimens of the juices of the *Agave Americana* collected at different times, for both of which we are indebted to Senor Manuel Guillen, of Mexico City, an extensive cultivator of the agave and producer of the "pulque" or fermented product of its juices. Senor Guillen, acting under directions from us, collected the fresh juices of the stalks of the agave plant, which were immediately evaporated in porcelain to a thick sirup and expressed to us in sealed bottles. Each of us has taken one of these samples which, it will be noted, contained the entire constituents of the juice of the agave, and, working separately, has isolated the sugar contained in it, and determined the characteristics of the same. Our results are given separately although practically identical with each other.

Sample A.—Received in June. The sirup on arrival contained a mass of large and well-developed crystals. The uncrystallized portion reduced Fehling's solution strongly. Of this specimen only the crystals which had formed on arrival were examined. They were separated from the sirup, and washed with dilute alcohol. They were nearly colorless, and had the characteristic appearance of sucrose crystals. After crushing and washing with alcohol the material was snow-white with a pure sweet taste. Examination showed :

1. The sugar was without effect upon Fehling's solution, but after warming with a few drops of acid it acquired a strong reducing power.

2. In 10-per cent. solution the sugar had a specific rotation $(\alpha)_D = 65.5^\circ$.

3. After inversion by warming with very dilute hydrochloric acid for thirty minutes at 65° the specific rotation was $(\alpha)_D = -20.1^\circ$.

4. The melting-point taken without special care in previously drying the material, was found to be 179° .

These results indicate plainly that the sugar under examination was sucrose.

Sample B.—Received in August. The material was a clear, brown sirup, free from crystals, but reducing Fehling's solution strongly. Upon concentration, the sirup crystallized and yielded upwards of 80 grams of brownish-colored crystals. These crude crystals, even after washing with alcohol, still contained enough of invert sugar to appreciably reduce Fehling's solution. The sirup was carefully concentrated until the last traces of crystallizable sugar had been separated. The residue was small in amount, reduced Fehling's solution strongly, and had a disagreeable taste, as might be expected from the presence in concentrated form of all the non-crystallizable constituents of the agave juice.

The different portions of crystals were united and recrystallized several times from both alcohol and water, care being taken to save all mother-liquors and washings. The final product was snow-white and finely crystalline, easily soluble in water, insoluble in strong alcohol at ordinary temperature, and very sweet. The material was systematically examined by all the well-known tests for identity, with the following results:

1. Specific rotation. In a 10-per cent. watery solution, the specific rotation was observed to be $(\alpha)_D = 66.3^\circ$.

2. Action on Fehling's solution. No reducing effect was observed beyond the slight action always noted when sucrose is boiled for some time with Fehling's solution and not exceeding that produced in a check-test with pure sucrose.

3. Melting-point. A test with samples crystallized from both water and alcohol checked against a sample of pure sucrose, gave in all three cases 183° to 184° .

4. When subjected to the action of ordinary yeast, fermentation was rapid and complete.

5. For a study of the behavior of the sugar by inversion, 2 grams of the material were dissolved in about 35 cc. of water to which was added 1 cc. of strong hydrochloric acid. The solution was kept in a water-bath at from 60° to 65° for thirty minutes, and was then neutralized with soda and filled up to a volume of 50 cc. The specific rotation was found to be $(\alpha)_D = -20.6^{\circ}$.

6. The reducing power of the invert sugar was determined by titrating the same into undiluted Fehling's solution and it was found that 4.94 mgms. of the invert sugar were necessary to reduce the copper in 1 cc. of Fehling's solution.

7. The phenylhydrazine compound prepared from this invert sugar melted at 203° .

8. The sugar when warmed with sulphuric acid, was immediately blackened and charred. Heated in solution with caustic soda it gave no brown coloration.

9. When warmed in solution with α -naphthol and strong hydrochloric acid a deep purple color resulted; with resorcin and hydrochloric acid, a cherry-red color.

It is apparent that the results of all these tests correspond strictly with the properties ascribed to sucrose, and that the results of two observers from two separate specimens are identical. The sugar thus studied is the only crystallizable sugar occurring in appreciable quantity in the juices of the *Agave Americana*. The possibility of any other sugar being present, aside from the invert sugar noted in the uncrystallizable portion of the sirup, is very remote. Messrs. Michaud and Tristan mention the occurrence of no other sugar save that which they describe as agavose, and there is no doubt that we have studied the same sugar as they, possibly in a purer state. That this sugar is sucrose seems also to be proved beyond doubt. For the present, therefore, the supposed new sugar, agavose, would seem to be a case of mistaken identity.

THE LAW OF MASS ACTION.

BY J. E. TREVOR.

Van't Hoff's famous derivation of the law of mass action from the principles of thermodynamics,¹ is essentially simple in character, but it involves an amount of machinery in the way of cylinders, pistons, and reservoirs, which is frequently found embarrassing when the subject is approached for the first time. The modification of this proof, which has been adopted by Nernst,² suffers from a similar disadvantage, and it requires, in some cases, the removal of a dissociating substance in undissociated form, thereby necessitating quite undue haste in the imagined experimentation. And both forms of the proof introduce the not entirely satisfactory feature of a completely semi-permeable wall, which can be employed in all cases.

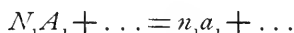
It would seem, therefore, not undesirable that the demonstration in question should be brought into a more simple and a more general form; although this must be done in the interest of simplicity of statement and not at all with the intention to cast discredit upon an idea which bears distinctly the mark of genius.

The law of mass action has hitherto found application only in the limiting case when the energy of the substances participating in a transformation is practically independent of their volume; that is to say, when these (gaseous or dissolved) substances are relatively dilute. In such cases the free energy of a change in concentration is proportional to the absolute temperature at which the change occurs, and the well-known relation

$$pv = RT \quad (a)$$

follows. The letters denote successively the actual pressure, the molecular volume, the gas-constant, and the absolute temperature.

Let us consider a chemical equilibrium established between the initial components A_1, A_2 , etc., and the products a_1, a_2 , etc., which they unite to form; the law (a) to hold for all constituents, and the equilibrium to be represented by the chemical equation

¹ Ztschr. phys. Chem., 1, 498 (1887).² Theoretische Chemie, 510.

At equilibrium the free energy F developable by this system must be a maximum, so for a virtual displacement in the positive direction of change

$$\delta F = 0$$

$$\delta F \equiv \sum n.v \delta p - \sum NV.\delta P = 0, \quad (1)$$

the two terms of the left-hand member of the equation being summated over all the initial components (capitals) and their products (small letters) respectively. The concentration relations which obtain at the equilibrium are sought; so the above differentials of the elastic energies of the reacting components must be expressed in terms of the respective molecular concentrations, which can be done with the aid of the governing relation $p v = RT$ between pressure and concentration.¹ The substitution yields

$$\delta F \equiv RT (\sum n \delta \log c - \sum N \delta \log C) = 0. \quad (2)$$

These values of c and C are the molecular concentrations in the state of equilibrium.

The work-value of the process, the limiting value of F for the change considered as occurring isothermally at its equilibrium, is obtained by integration of this virtual change over the entire transformation of n_i , etc., mols,

$$F = RT \int (\sum \partial \log c^n - \sum \partial \log C^N) \quad (3)$$

the constant of integration disappearing from the definite integral. This becomes

$$F = RT \log K \quad (4)$$

when the change is conducted in the positive direction and K is set for the ratio $\Pi c^n / \Pi C^N$. And since F must be constant for a given isothermal change this ratio must be constant also, —which is the law of mass action.

The value (4) of the chemical affinity F must be clearly distinguished from the actual free energy Φ developed by the process when the initial state includes none of the products of the reaction. Φ is the free energy of the change as it actually

¹ In this process we eliminate $v = RT/p$ and set dc for the dp , to which it is proportional; or we eliminate $dp = -(RT/v^2)dv$ and replace the molecular volume by its reciprocal, the molecular concentration; or we write (1) as $\delta F \equiv \sum N.p \delta V - \sum n.p \delta v$ and eliminate $p = RT/v$, replacing v by $1/c$; or eliminate $dv = -(RT/p^2)dp$, replacing dp by dc . The transformation is the same in each case, except that in the first and last modes the condition of constant temperature is introduced. The writer prefers the third mode.

occurs, while F is the limiting value obtaining at equilibrium; Φ is the affinity to which the formation of the resultant mixture of substances is due; F is the affinity which the two reacting systems have for each other in this mixture.

The disturbing influences of variations in temperature are then pursued in the usual way, by partial differentiation of (4) to obtain

$$RT \cdot \frac{\partial \log K}{\partial T} = \frac{-E}{T};$$

— E signifies the energy difference of the two reacting states.

CORNELL UNIVERSITY, *January, 1895.*

CHROMATES OF THE RARE EARTHS: CHROMATES OF THORIUM.¹

BY CHASE PALMER.

Believing that a study of the action of an acid of feeble energy upon the weak bases of the tin group—or Fourth Group of Mendeléeff's Periodic System—would throw new light upon this interesting family of elements, I have undertaken a comparative study of the action of chromic acid upon the oxides of the rarer metals of this group, and of the conduct of their salts towards the alkaline chromates.

The chromates of the rare elements of this group have hitherto received but little attention from chemists. The earliest allusion to a chromate of a rare earth was made in 1863 by J. J. Chydenius.² This author observes that thorium hydroxide is soluble in chromic acid. He states that from the resulting solution, evaporated over sulphuric acid, he obtained normal thorium chromate as a soluble salt containing 8 molecules of water of crystallization. Chydenius further states that potassium dichromate produces no precipitate when added to a solution of thorium chloride, until after the mixture is neutralized with ammonia, whereby a basic salt of thorium is thrown down. The only other allusion to a chromate of a rare metal of the Fourth Group, in the literature accessible to me, is made by Pattison and Clarke.³

¹ I wish to express here my hearty thanks to Professor Edgar F. Smith, through whose generous hospitality I have enjoyed the facilities of the John Harrison Chemical Laboratory of the University of Pennsylvania, where the work described in this paper has been done.

² "*Thorerde und deren Verbindungen*:" *Ann. der Phys. Pogg.*, **119**, 43.

³ *Chem. News*, **16**, 259.

These chemists observed that by heating the residue from an evaporated solution of the hydroxides of cerium, lanthanum, and didymium in chromic acid, the cerium compound was rendered insoluble; but there is no evidence that they determined the composition of the insoluble product.

Thorium was chosen as the first element for the present research on account of the highly developed basic properties of its oxide. Contrary to the observations of Chydenius, I have found, not only that a difficultly soluble salt, having the composition of normal thorium chromate, separates spontaneously from a solution of thorium hydroxide in chromic acid, but also that the same compound is precipitated by potassium dichromate from thorium nitrate without the aid of a neutralizing alkali. I have also found that potassium chromate produces the same compound indirectly from a soluble thorium salt.

Thorium Hydroxide and Chromic Acid.—Pure, freshly precipitated thorium hydroxide was added in portions to a solution of pure chromium trioxide in water. The quantity of the trioxide was slightly in excess of the amount required to form the normal chromate. The hydroxide was quickly dissolved at first, but afterwards the acid attacked it more sluggishly. A flocculent orange precipitate soon appeared, and finally settled as a fine powder. Under the microscope this product shows a crystalline structure. The formation of the orange precipitate takes place more quickly at 90° C. than at the ordinary temperature.

Dried at 120° C. to constant weight the product was analyzed:

0.2016 gram substance at 180° lost 0.0072 gram H₂O and gave 0.1114 gram ThO₂ and 0.0626 gram Cr₂O₃.

	Calculated for Th(CrO ₄) ₂ ·H ₂ O.	Found.
H ₂ O	3.73	3.57
Th.....	48.05	48.55
Cr.....	21.71	21.29

Thorium Chromate from Chromic Acid Solution.—Pure, freshly precipitated thorium hydroxide, in small portions at a time, was stirred in a cold solution of chromic acid as long as

it was taken up. At the first appearance of the orange precipitate, the latter was filtered off, and the solution evaporated over sulphuric acid *in vacuo*. From the concentrated solution thorium chromate separated out in orange-colored scales containing 2 molecules of water of crystallization and 1 molecule of water of constitution.

Dried to constant weight over sulphuric acid the salt was analyzed:

I. 0.215 gram substance lost 0.0148 gram H_2O at 120° ; at 180° it lost 0.007 gram H_2O additional, and gave 0.1104 gram ThO_2 and 0.0631 gram Cr_2O_3 .

II. 0.2155 gram substance lost 0.015 gram H_2O at 120° ; at 180° it lost 0.0068 gram H_2O additional, and gave 0.111 gram ThO_2 and 0.0622 gram Cr_2O_3 .

	Calculated for $Th(CrO_4)_2 \cdot 3H_2O$.	I.	Found. II.
$2H_2O$	6.90	6.88	6.96
H_2O	3.46	3.25	3.15
Th.....	44.71	45.12	45.26
Cr.....	20.20	20.12	19.70

Thorium Nitrate and Potassium Dichromate.—On mixing the boiling solutions of these salts in the proportion of 1 molecule of the nitrate to 2 molecules of the dichromate, hydrated thorium chromate was precipitated at once as a fine orange powder. In this way 78 per cent. of the theoretical yield was obtained.

0.1986 gram substance, dried at 120° , lost 0.0073 gram H_2O at 180° and gave 0.1095 gram ThO_2 and 0.0068 gram Cr_2O_3 .

	Found.
H_2O	3.67
Th....	48.35
Cr.....	21.34

When the cold solutions of thorium nitrate and potassium dichromate were mixed no immediate precipitation occurred, but in a short time a precipitate began to form. After standing twenty-four hours the orange precipitate that had formed meanwhile was filtered off, washed, and dried at 120° .

0.1817 gram substance lost 0.0064 gram H_2O at 180° , and gave 0.1008 gram ThO_2 and 0.0569 gram Cr_2O_3 .

	Found.
H ₂ O	3.52
Th	48.75
Cr	21.47

The filtrate from this precipitate was heated to 90°. At 60° a second precipitation of the thorium chromate occurred. The first yield was 65 per cent., and 14 per cent. additional was obtained by heating the filtrate. The total yield (79 per cent.) closely corresponds with the yield obtained by precipitating the compound at once from a boiling solution.

The mother-liquor from the second precipitate was reduced to small volume, but no further precipitation occurred. By evaporating it to dryness a very soluble crystalline product was left, but it could not be isolated for examination.

Thorium Nitrate and Potassium Chromate.

There are two stages in the formation of hydrated thorium chromate from thorium nitrate and potassium chromate. When a solution of thorium nitrate is treated with a solution of potassium chromate (one molecule of the former to three molecules of the latter) the precipitate, which at once forms, dissolves immediately until the mixture is complete. Then a dense golden-yellow precipitate separates from the solution. The liquid meanwhile becomes red, owing to the formation of potassium dichromate. By promptly removing the yellow precipitate from contact with the fluid it was found, on analysis, to be basic thorium chromate.

0.2367 gram substance dried at 100° gave 0.1635 gram ThO₂ and 0.0459 gram Cr₂O₃.

	Calculated for Th(OH) ₂ CrO ₄ .	Found.
Th	60.66	60.70
Cr	13.70	13.29

If the basic thorium chromate be allowed to remain in contact with the supernatant liquid, it is gradually changed into the orange precipitate which, upon analysis, proved itself to be the same hydrated thorium chromate already described. During this transformation the red liquid is changed to the bright yellow color of potassium chromate.

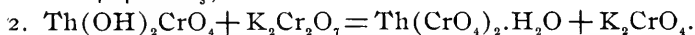
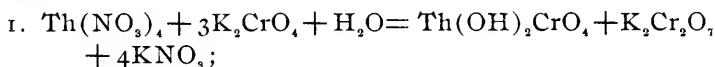
Analysis of the final product dried at 120°.

0.2136 gram substance at 180° lost 0.0081 gram H_2O and gave 0.1175 gram ThO_2 and 0.0678 gram Cr_2O_3 .

Found.

H_2O	3.79
Th	48.34
Cr.	21.77

The complete reaction may be expressed by the two equations:



The hydrated thorium chromate always has a full orange color, which it does not lose even after prolonged heating at 130° . The color of the anhydrous salt is ochreous yellow. At 22° , 1 part of the salt is soluble in 284 parts of water. It is readily soluble in hydrochloric acid and in ammonium carbonate. At a dull red heat it is decomposed into thorium dioxide and chromic oxide. Heated in a platinum crucible over a Bunsen lamp the substance lost 10.41 per cent. in weight. For the loss of three oxygen atoms to form ThO_2 and Cr_2O_3 , the required loss in weight is 10.32 per cent.

Constitution of the Orange Chromate.—It is noteworthy that the orange chromate of thorium always contains one molecule of firmly bound water, whether the substance be formed by slow crystallization from a chromic-acid solution, or by precipitation from a soluble salt, or formed from the insoluble basic chromate. The substance may be regarded simply as hydrated normal thorium chromate ($Th(CrO_4)_2 \cdot H_2O$), or it may be a basic dichromate of thorium having the constitution expressed by the formula $Th \begin{smallmatrix} < Cr_2O_7 \\ (OH)_2 \end{smallmatrix}$.

Before expressing an opinion as to the more probable constitution of the orange chromate, I shall attempt to gather more knowledge of these chromates and of the compounds of chromic acid with the related elements.

Zirconium hydroxide is attacked by chromic acid less readily than is thorium hydroxide. It can be completely dissolved in an excess of the acid. A yellow precipitate was obtained

by boiling this solution. From an analysis, the product appears to be a basic salt.

A similar yellow precipitate is obtained by the action of potassium dichromate on zirconium chloride. The precipitate, dried over sulphuric acid, gave 41.24 per cent. Zr and 16.38 per cent. Cr. It is probably a basic salt.

I intend to make a thorough study of the chromates of zirconium and of the other elements of the Fourth Group.

ON A NEW METHOD FOR THE SEPARATION OF COPPER AND CADMIUM IN QUALI- TATIVE ANALYSIS.

BY ALLERTON S. CUSHMAN.

The successful separation of small quantities of cadmium from copper has been one of the difficult operations of qualitative analysis. The method depending upon the solubility of copper sulphide in potassium cyanide, is not considered by most chemists so desirable as the method of boiling the mixed sulphides in dilute sulphuric acid, on account both of its inferior delicacy, and of the unpleasant character of the reagent. The last edition of Crookes' "Select Methods in Chemical Analysis," has to say on this subject: "Cadmium sulphide dissolves with the greatest facility in boiling dilute sulphuric acid, which has no action on copper sulphide. On precipitating, by sulphuretted hydrogen, a solution containing not more than 1 milligram of cadmium mixed with 1000 milligrams of copper and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part concentrated acid and 5 parts of water), a colorless filtrate is obtained in which an aqueous solution of sulphuretted hydrogen produces an unmistakable precipitate of yellow cadmium sulphide. Another solution of the same composition was mixed with an excess of potassium cyanide and treated with sulphuretted hydrogen gas. A distinct yellow coloration was observed; a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in potassium cyanide also gives rise to a yellow coloration when submitted to the action of sulphuretted hydrogen."

Undoubtedly the sulphuric-acid separation is an exceedingly delicate one, when performed under the conditions detailed in the foregoing. When, however, the amount of copper present is large, and the filtration of the mixed sulphides is prolonged, traces of copper are almost certain to find their way by oxidation into the sulphuric-acid solution, in which case, on addition of hydrogen sulphide, the yellow color of the cadmium sulphide is invariably masked by the brown tinge of the sulphide of copper. Very small quantities of cadmium dissolved in an excess of dilute sulphuric acid may very easily escape detection on further dilution and addition of hydrogen sulphide unless extreme care, cleanliness, and rapidity in filtration have been observed. Certainly few metals oftener escape detection in elementary practice than does cadmium when present in small quantity with copper.

In the solutions that were given out for analysis to the students in this laboratory, it was noticed that when cadmium and antimony were present in the same solution, the cadmium frequently failed to be precipitated by hydrogen sulphide out of acid solution, but made its appearance with the precipitates of Groups III–IV. It seemed that the only explanation of this lay in the fact that a strong solution of sodium chloride had been added to each mixture in which antimony was put, in order to prevent the separation of basic compounds of the latter metal. In the course of an investigation bearing upon this subject, it was found that when cadmium sulphide was treated with a saturated solution of one of the alkaline chlorides in the presence of dilute hydrochloric acid, it immediately dissolved to a clear solution with evolution of hydrogen sulphide. As far as can be learned this reaction between cadmium sulphide and solutions of the alkaline chlorides in the presence of dilute hydrochloric acid has been nowhere noted. The ability of the alkaline chlorides to form double salts with many of the metals is well known, and according to V. Hauer, cadmium chloride unites with the alkaline chlorides and chlorides of the alkaline earths to form compounds of the general formulae: $4\text{RCl}, \text{CdCl}_2$; $2\text{RCl}, \text{CdCl}_2$; $\text{RCl}, \text{CdCl}_2$.¹ On boiling cadmium oxide and cadmium car-

¹ Pharm. Centralbl., 1858, 292, 787; 1856, 766.

bonate with ammonium chloride solution a double crystalline compound has been obtained with the formula $2\text{NH}_4\text{Cl} \cdot 2\text{CdCl}_2 \cdot \text{H}_2\text{O}$.¹

In order to see if a strong neutral solution of ammonium chloride had any action on cadmium sulphide the following experiment was made: A solution of cadmium nitrate was precipitated by hydrogen sulphide, and the precipitate thoroughly washed by decantation with boiling water until free from last traces of sulphuretted hydrogen. The precipitate was then thrown on a filter, sucked dry, and finally dried at 100° . A quantity of this dried cadmium sulphide was suspended in a concentrated solution of ammonium chloride in a flask which was connected with a Varrentrapp-Will tube containing a solution of lead acetate. The temperature of the mixture was then gradually raised without producing any precipitate in the bulb-tube until protracted boiling had taken place, when a decided precipitate of lead sulphide appeared in the tube. It is a well-known fact that solutions of ammonium chloride become acid on prolonged boiling owing to dissociation and escape of ammonia.² As the partial reaction in this case only began after prolonged boiling it is probable that it was due to the formation of free hydrochloric acid in the solution. On addition of dilute hydrochloric acid to the mixture in the flask, the cadmium sulphide immediately dissolved. On repeating the foregoing experiment using sodium chloride instead of ammonium chloride, no hydrogen sulphide was given off except in the presence of free hydrochloric acid. In a general way the reaction is perhaps best expressed by the following: $\text{CdS} + 2\text{RCl} + 2\text{HCl} = \text{CdCl}_2 + 2\text{RCl} + \text{H}_2\text{S}$.

This solubility of cadmium sulphide in acidified concentrated solutions of the alkaline chlorides, renders possible an exceedingly delicate method of testing for cadmium. If to 2 cc. of a solution containing a small amount of cadmium, 10 cc. of a saturated solution of salt and a few drops of dilute hydrochloric acid be added, hydrogen sulphide fails to produce any precipitation even up to saturation of the liquid by the gas. If now a few drops of dilute ammonia be allowed to flow down

¹ Graham Otto, Aufl. 5, III., 828.

² Ann. Chem. (Liebig), 128, 189; Graham Otto, III, 485.

the side of the tube a distinct yellow ring or layer of cadmium sulphide appears at the junction of the two liquids. By this method 1 cc. of a solution containing 0.1 milligram of cadmium sulphate developed a distinct yellow ring in a few minutes, while three drops of the same solution, equal to an amount less than 0.01 milligram of cadmium, developed a perceptible ring on standing half an hour.

The fact that copper sulphide has been found quite insoluble in the reagents, offers an easy and delicate method of separating the two metals. When the metals are present in comparatively large quantity it is only necessary to treat the mixed sulphides with an excess of a strong solution of salt and a little dilute hydrochloric acid, when, on warming, the cadmium sulphide entirely dissolves. On dilution of the filtrate and addition of hydrogen sulphide, the cadmium sulphide is re-precipitated. The method is more accurately carried out in this laboratory as follows: About 2 cc. of the solution containing the two metals is made slightly acid with hydrochloric acid and about 20 cc. of a saturated salt-solution added, the solution warmed, and hydrogen sulphide passed through until the copper is all precipitated and the hydrogen sulphide is present in excess. The copper sulphide is then filtered off through a dry filter, and the filtrate run into a dry test-tube. The filtrate collected in the tube should be perfectly clear, as the slightest dilution begins to precipitate the cadmium. Therefore if a few drops of water be allowed to run down the side of the test-tube, a yellow line will be formed at the junction of the two liquids if cadmium is present. Diluted ammonia may be substituted for water with advantage if the amount of cadmium present is very small, as it develops the yellow layer more rapidly than water does. On the other hand if traces of other metals are present through incomplete removal in the group separations, the result will be obscured by the use of ammonia.

This method has been thoroughly tested with mixtures of solutions of copper and cadmium in varying proportions, and has been found extremely sensitive. Sometimes it has been found that, when very minute quantities of copper are present, the copper sulphide is precipitated in the strong solution of

sodium chloride in so finely divided a condition that it is impossible to remove it completely by filtration. In this case the addition of a few drops of a solution of copper sulphate, and re-precipitation with hydrogen sulphide obviates the difficulty.

In the hands of students the method has given uniformly good results when carried out with the ordinary care necessary to the success of all analytical processes. As some other metallic sulphides, notably those of lead and bismuth, are found to be soluble in strong acidified solutions of the alkaline chlorides, these metals must be as completely removed as in any other test for cadmium.

The bearing of these reactions with lead, bismuth, and cadmium sulphides on qualitative and quantitative separations, will be more fully studied in this laboratory in the future. The simplicity of the reagents used, and the delicacy of the test for cadmium will probably commend the method to chemists and instructors in qualitative analysis.

ST. LOUIS, MO., Feb. 27, 1895.

REVIEWS.

GERMAN OFFICIAL REPORT ON CHEMICAL INDUSTRY AT THE CHICAGO EXHIBITION OF 1893. Dr. OTTO N. WITT. *Die chemische Industrie auf der Weltausstellung zu Chicago, und in den Vereinigten-Staaten von Nord-Amerika, in 1893.* Berlin, 1894.

The author of this report, who is Professor of Chemical Technology at the Royal Technical High School of Berlin, in his visit to the United States in the summer and autumn of 1893, set before himself two objects—a study of the products of chemical industry exhibited at Chicago, and an examination of the present state and future prospects of chemical manufactures in this country.

While acknowledging with gratitude the obliging readiness of individual exhibitors, and of those connected with American manufacturing establishments, to afford information, he makes more than one significant allusion to defects of management which marred the Chicago exhibition for thoughtful students of it as a serious display of the world's work—the imperfection with which much of the pretentious plan was carried out, the difficulty of finding many things scattered among the huge buildings, the uselessness of the official general catalogue, the poor light in large portions of the space devoted to

exhibits, etc., etc. He found but three countries at all worthily represented in the field of chemical industry—namely Germany, the United States, and Japan—and felt most interest in the contrast presented by his own country, of originally limited resources, but now possessing the most highly developed chemical manufactures, with the United States, gifted by nature with resources in the way of raw material wonderful in extent and variety, but barely beginning to develop and utilize them.

Some very important branches of industry dependent upon chemical principles, including some that have become well established in this country and owe much in the way of improvement to American skill and enterprise, are excluded from consideration in the report. Thus metallurgical processes, and all those processes more or less closely connected with food, such as the preparation of sugar and starch, brewing, distilling, etc., are omitted. The subject is treated under three main heads—fuel, inorganic chemical products, and chemical products of organic origin or character.

Under the first head there is a condensed account of American petroleum, its varieties, distribution, extraction, and refining, including some comparison with the treatment of the analogous Russian product, and some notice of its special value as heat-producing fuel in certain manufacturing operations. Attention is drawn to the mineral oil distilled at Sydney from the bituminous shale of New South Wales, this shale being reported as existing on quite a large scale.

In noticing the abundance of coal in the United States and its immense importance for the future, with which the author was greatly impressed, he finds it least troublesome to mention the States only (9 in number) in which workable coal has *not* been found. He observes the less depth of most American coal mines than of those in Europe, and hence in part the superior cheapness of the product—also the freer choice between anthracite and bituminous coal over a large part of the country. He comments on the occurrence of the most valuable coal beds in the regions comparatively near the Atlantic coast, while the coal of the interior of the continent is for the most part of more recent age and poorer in quality, and concludes from this difference that to the Atlantic States belongs, in the main, the future of chemical manufacturing on the great scale. He did not see any sign of efforts to secure smoke consumption, and was surprised to find so little progress toward saving the by-products (tar and ammoniacal liquor) of coking bituminous coal, as is now quite successfully done in the Rhenish provinces and in Silesia. He understands that the great extension of electric lighting, and the general use in the larger

cities of the United States of "water-gas"¹ instead of coal-gas proper for illuminating purposes, offer little prospect of tar and ammonia products growing in importance in the future, although the Solvay-process soda-works at Syracuse, N. Y., have started an experimental set of Semet-Solvay coke ovens, saving the by-products. Hence the outlook for American competition in the multifarious chemical industries based upon the constituents of tar does not at all alarm the German observer. It would seem, however, that the enormous demand in this country for fertilizers of all kinds, including the nitrogenous, ought to lead the managers of the great Pennsylvanian and West Virginian coke works to look carefully into this question of saving the by-products obtainable by some of the more modern types of ovens. If the day has not yet come, or perhaps may never come, for rivalling here the great German factories for coal-tar colors, medicinal agents, artificial perfumes, etc., it does not seem certain that crude benzene, toluene, anthracene, phenol, and the like, might not be made with profit on a large scale in America, by first distillation of tar, if the tar itself were saved in adequate quantity to build up a large business.

The reporter comments, as so many others have done before him, on the reckless destruction of wood in the great forest-covered regions of the United States. He notes the fact that the dry distillation of wood, yielding acetic acid, methyl alcohol, and acetone, is carried on in this country; but this industry was not represented at the Chicago exhibition, and he apparently did not hear of some interesting peculiarities which American works have developed in connection with it.

As respects the prime natural materials for chemical industry on the great scale, Dr. Witt does not consider the United States so highly favored as Europe. He notes the fact that this country is now the greatest consumer of sulphur (as such) in the world, pointing out that in 1889 there was imported from Sicily three times as much as was taken by England in the same year, some moderate amount coming in from Japan at San Francisco, a few hundred tons only of domestic sulphur being supplied by California, Nevada, and Utah, and none yet furnished by the great Louisiana bed in Calcasieu Parish, which is so far known only by borings. The reporter seems to look for little increase in the use of pyrites for making sulphuric acid, observing that only Massachusetts and Virginia furnish pyrites in any important quantity, but on this point he probably underrates the influence of present commercial conditions favoring the use of native sulphur, and the pos-

¹ The reporter is severe in his allusion, later on, to the recklessness with which illuminating gas of such highly poisonous character is admitted to dwellings in America.

sibilities of the future in the way of larger supply of pyrites (as from Georgia, New York, and some of the Western States) under the stimulus of increased demand. He not unnaturally speaks of rock salt in the United States as a small affair in comparison with the vast European deposits at Stassfurt, Wieliczka, etc., but hardly does justice to the extent of production of American boiled salt for the country at large, though he describes with interest the many square miles of shallow wooden tanks at Syracuse for evaporation of brine at atmospheric temperature, and notices the exhibit at Chicago of boiled salt from the Great Salt Lake of Utah. Mention is made of "*Abraumsalz*" (Kainite) as shown from the Louisiana salt bed on Petit Anse island, but it may be questioned whether there was not some mistake about this. It is conceded that American limestone is abundant and widely distributed. Manganese ore is said to be chiefly used in this country for decolorizing glass, but this statement seems to ignore the great scale on which it is now called for by the large steel works. It is stated that large quantities of oxide of manganese in the form of "Weldon mud" are imported into the United States and used in coloring tiles and terra-cotta blocks in imitation of, or to harmonize with, "brownstone." Notice is taken of the native carbonate and sulphate of soda from Wyoming as interesting American specialties. The only worthy exhibits of crude chemical materials from Europe were those of English salt and German (Stassfurt) potash and magnesia compounds.

There was practically no general display at Chicago illustrative of the production of acids and alkalies on the great scale. Notice is taken of the extensive use in America of Sicilian and "regenerated" sulphur for making sulphuric acid, and the consequent greater freedom of the acid than in Europe from arsenic, making easier the production of pure hydrochloric and nitric acids. The great demand now for bicarbonate of soda, growing out of the widespread use of "baking powders" and the large consumption of soda-water, and the more frequent use than in Europe of carbonate of soda instead of sulphate of soda for glass-making, are facts shown to bear strongly on the question of the alkali industry becoming established on a great scale in America. Few facts in regard to chemical manufactures are more remarkable than that this has not yet taken place. Notice is taken of the ammonia-soda works at Syracuse, N. Y., operating under the Solvay patents, but making no separate exhibit of the product, which was shown in the French department, and very favorable comment is made on the cryolite-soda works of Natrona, Pa., the special *raison d'être* for which is taken to be the large demand in the United States for aluminium salts for

paper-making, dyeing, etc., with relative scarcity of bauxite; the Natrona establishment is spoken of as a good example, "the only one in America," of an undertaking in the way of large chemical manufacture well devised to meet actual conditions, complete in itself, and working up all by-products. Dr. Witt does not seem to have heard of the large alkali works which are being built at Saltville in South-western Virginia, at which it is proposed to operate on both the Leblanc and the ammonia-soda plans. An extended account is given of the exhibit made at Chicago in the English section by the great "syndicate," (formed in 1890), known as the United Alkali Co., the largest joint stock chemical manufacturing company in the world, with a total capital of nearly £9,000,000 sterling, uniting 45 great chemical factories, 3 salt works, 2 soap factories, and 1 rosin refinery. Attention is drawn to several of the special products of this company, such as the very convenient caustic soda *in powder* (pulverized in closed mills, excluding the air), the "crystal carbonate of soda" (crystallized hot, with but a single molecule of water of crystallization) which has the advantage over ordinary soda crystals of greater concentration and offers an equal guarantee of purity, the sodium chlorate (with greater solubility than that of potassium chlorate) for print works, the barium chlorate giving aniline chlorate by interaction with aniline sulphate, the sodium manganate for use as a cheap disinfecting material, the finely pulverulent chromium trioxide in air-tight packages for Bunsen batteries, and the regenerated sulphur from the Leblanc process, of which 40,000 or 50,000 tons a year are produced, much of which finds a market in the United States to be again converted into sulphuric acid.

Ammonia-soda appeared at the exhibition not only from the Solvay works in France (*Varangéville-Dombasle*), but from English and Russian establishments.

Under the head of materials used as manures it is remarked that Germany holds essentially a monopoly of potash salts; that the United States depends for nitrogenous material upon South American nitrate of soda and European sulphate of ammonia, neglecting the advantages offered by modern coke ovens for saving the nitrogen of coal, but that to this country must be conceded the first place in the supply of phosphates. The reporter fully recognizes the great importance of the phosphate deposits of South Carolina and Florida, especially the latter, which he visited and gives some description of.

The extent and importance of the American manufacture of glass are noted, though this industry was very poorly represented at Chicago. The reporter was impressed by the good results of using (since 1880) furnaces fired with natural gas, and also with artificially prepared gaseous fuel ("generator"

gas), the high and easily controlled temperature of these furnaces having regenerative chambers on the Siemens principle being very advantageous. The development in this country of the manufacture of *pressed* glass is favorably noticed. The great European glass works were unrepresented at the Chicago exhibition, with the exception of a handsome display of Bohemian ornamental glassware. Notice is taken of the important improvements made of late in Germany in the composition of glass for various scientific purposes, the Jena glass for optical instruments, for thermometers, and for chemical laboratory vessels (resisting ordinary liquid reagents to a remarkable extent)—and it is observed that Japan for the first time sent forth glass of her own manufacture.

Clay-ware was much better shown than glass at Chicago, and the reporter seems to have felt especial interest in the details of some of the methods by which more or less new results were obtained. Mention is made of a new porcelain-ware introduced at the Royal Porcelain Factory of Berlin, which is very refractory and becomes, not denser, but more porous in the firing—valuable for removal by filtering of bacteria from water, for porous diaphragms in electrolysis, etc. There is an interesting account of Japanese clay work, including mention of "*Kaga*" (hard porcelain) figures formed, not in molds, but by free-hand sculptor's modeling. In connection with the chemistry of clay-ware, the extensive use in the United States of Weldon mud for coloring terracotta, and the free addition of precipitated barium carbonate to prevent efflorescence, receive notice.

Under the head of chemical apparatus and appliances, the very handsome displays made by Heroeus of Hanau, and Johnson and Matthey of London, of platinum apparatus, the rare platinum metals and their salts, etc., are spoken of with deserved admiration.

Among the smaller and finer products of chemical manufacture the two most interesting novelties noticed were both American; *viz.*, the oxides and salts of the rare earthy metals, thorium, zirconium, yttrium, lanthanum, etc., prepared from North Carolina monazite, zircon, etc., and used by the Welsbach incandescent gas-light company, in regard to which it is noted that the higher temperature afforded by "natural gas" gives a better light from the wicks made by skeletons of these metallic oxides than when artificial "water-gas" is used,—and the new carbide of silicon, or "carborundum" made by Acheson, of Pennsylvania, from sand, coke, and a little common salt intensely heated in an electric furnace. As to the value as an abrasive of this material the reporter states, on the authority of Dr. A. Miethe, that its effect upon glass is 9 times that of the best emery. Mixed with 30 *per cent.*

of refractory clay, carborundum is molded into cutting and polishing wheels, and burned in a small porcelain kiln. There is a rather comical notice of the wonder with which were regarded the light color and inalterability of sticks of phosphorus exhibited by J. J. Allen's Sons, of Philadelphia, explained by the fact that for safety's sake the sticks exhibited were made of paraffine! The brief mention of bromine from Pomeroy, Ohio, and of California borax, does not seem to indicate adequate appreciation of the capabilities for production of the regions in question. It is remarked, and certainly with entire justice, that by far the most extensive and complete exhibition of chemical preparations was that made by Germany—in fact no other country made anything like a worthy display. Among the novelties included in the German collection special mention is made of potassium cyanide free from cyanate, made by acting with metallic sodium on the ordinary cyanide, and intended for use in the metallurgical extraction of gold, and notice is also taken of piperazine, so highly recommended of late as a solvent for uric acid.

The reporter found at Chicago little that was new or worthy of special mention in connection with dyeing or calico-printing. He mentions with interest some Japanese ornamental work on silk, in which the effect was produced by a combination of printing and free-hand painting. This union of block and brush work is of great antiquity (upon cotton) in India. There was but a poor display of textile materials—it is observed as particularly disappointing that so insignificant an exhibit of raw cotton should have been made by the greatest cotton-producing country of the world.

The comparatively small use of candles in the United States is remarked, and the absence at the exhibition of much that was new in the manufacture of candles and soap, though there was a good deal of both products to be seen, especially of the latter. Favorable mention is made of the excellent glycerine made by Jas. S. Kirk & Co., of Chicago, from the underlye of salted-out soap, by evaporating, crystallizing out most of the salt (to be used over again), precipitating the last remains of the fatty acids in the form of insoluble salts of calcium and aluminium, and distilling the glycerine under much-reduced pressure.

As a whole the report is interesting—more so than might have been expected from the inadequate and irregular way in which the chemical products of the world's industry were exhibited at Chicago. Some new things that either have already attained importance, or seem likely to soon become important, are left without notice. Silver refining and copper refining by electrolysis are omitted, perhaps as metallurgical processes, but it is surprising to find no discussion of the

attempts being made to decompose common salt and potassium chloride by the electric current, and so to manufacture by more direct methods than those now in use, the caustic alkalies and alkaline carbonates, bleaching-powder, chlorate of potash or soda, etc. Nor is there any notice of the production in the electric furnace of calcium carbide to be used in the production of acetylene for carbureting or enriching illuminating gas (this has been going on in North Carolina for a year or two past). In the thoughtful discussion of *American* chemical industry—present and prospective—it may fairly be said that the greatest omission is that of any notice of the baneful influence in this country of *vacillation in legislation* on commercial and industrial matters. However people may differ in their views of public policy in respect to such matters, there is no room for doubt that *uncertainty* is the worst of all public enemies to industrial enterprise, and from this the United States has suffered much in the past, and seems to have little chance of exemption in the future.

J. W. M.

FRENCH OFFICIAL REPORT ON CHEMICAL INDUSTRY AT THE CHICAGO EXHIBITION. M. HALLER. Rapport du Comité 19; Produits chimiques et pharmaceutiques, matériel de la peinture, parfumerie, savonnerie;—Paris, 1894.

In this report we have a view of the present condition of chemical industry, its novelties, and its prospects for the future, from a standpoint not the same with that occupied by Dr. Witt, and it presents much that is thoughtful and worthy of study.

Noticing the United States as a country of great but very imperfectly developed resources, among which he counts abundant water-power for the future extension of electrolytic processes under favorable conditions, the reporter considers Germany, England, and France as the great seats of chemical manufactures for the supply of the world at large, and contrasting the progress of these three, for the last fifteen or twenty years, he recognizes that Germany has advanced most rapidly, her gain in position being most marked within the period named, for which he examines the statistics in some detail, but dating back to the middle of the century, to the era of the birth of structural and so-called synthetic organic chemistry. He finds the causes of German success in the practical, rather than idealistic, character of the Germans, their talent for organization, and their habits of discipline, which render possible combined effort on a large scale in industrial enterprises, and in illustration he points to the value of the "Syndicate of Chemical Industry" in the united influence it has brought to

bear upon legislation as to patents and in other directions. But he lays especial stress upon the importance of German organization of scientific thought, education, and research. He is deeply impressed by the force gained from freedom in teaching, freedom in learning. He sees in the professor of a German university, not merely a medium for the transfer to pupils of already acquired information, but a former of minds and a pioneer of knowledge, a man whose best recommendation to official appointment and to promotion has been his reputation for original work, who has placed at his disposal the most ample material appliances for work, and who, as a scientific man, is more highly regarded and enjoys more social consideration in his own country than anywhere else in Europe. The writer points out the close connection established in Germany between the industrial application of scientific knowledge and the continued extension of that knowledge, so that there manufacturing chemistry, *including research*, offers a career to the scientific chemist who has been trained at a university, and quotes the fact that 4 of the largest German firms among them give constant employment to more than 230 chemists, a large proportion of whom are engaged solely in original research. German industrial success has been most conspicuous in the directions in which scientific chemistry has made most rapid progress, in organic chemistry, in the production of the coal-tar colors, of medicinally used chemicals, of artificial perfumes, of explosives.

England holds, as her main strength, to the production of the simpler mineral chemicals in gross, the manufacture of acids, alkalies (or rather alkali, since the possession of the unique Stassfurt deposits gives Germany essential control of the production of potash) and mineral salts. It is remarked that in England chemists with more or less scientific training are employed by manufacturing firms, but not to any great extent for purposes of research, and that they are, as a rule, but poorly paid. There might have been added unfavorable comment upon the ill effects of the reign of examinational cramming which has borne heavily upon English scientific education for the last quarter of a century or so, though vigorous protests against it are not lacking from some of the most competent English sources.

M. Haller, himself Director of the Chemical Institute of the Faculty of Sciences of Nancy, finds much to lament in regard to the falling back of France in the race for success in chemical industry, and in regard to the causes which seem to him to be concerned in this. He regrets the failure to revise legislation on the subject of patents since 1844, the exorbitant tax upon the alcohol which is so much needed in modern organic chemistry, but, above all, what he considers serious defects in

respect to scientific organization and scientific education. He quotes the clear-cut words of Taine on the deadening effect on higher education of the spirit of authority, and of fixed rule and programme, ending with exhaustive and exhausting examinations; the human product thus characterized: "Leur vigueur mentale a fléchi; la sève féconde est tarie; l'homme fait apparaît, et, souvent c'est l'homme fini."

Scientific education in the United States is not spoken of by the reporter at much length; probably his opportunity of examining it for himself was not very ample; but it seems to him, more than in Europe, and solely because of the conditions belonging to a new country, "d'un caractère trop positif, trop pratique, trop immédiatement utilitaire en un mot, pour qu'il puisse donner tous les fruits qu'on est en droit d'en attendre." What is said in expressing a desire for new establishments for higher scientific education in France, deserves attention in this country, that there is danger by multiplying too much such establishments of lowering the grade of instruction, and of the results attained—there is only a moderate amount of sound human material, professors and students, leaders and led, available in the country at any one time for higher education in the proper sense—and concentration of this, to a reasonable extent, is surely desirable. Those who have seen much of American educational work can hardly fail to recognize among its weak points a good-natured readiness to be not too critical, but to pass over lightly the confusion of real with self-claimed merit, and to allow every school to call itself a college, every college a university, without its being a part of anyone's business to draw over-nice distinctions on such questions. No doubt much of this will remedy itself in time, and those who can look back thirty or forty years have already seen great improvement.

Under the head of "Produits de la grande industrie chimique," the reporter has an interesting discussion of the question whether the electrolytic decomposition of common salt is soon to become the mode of utilizing its constituent elements, with both of which—sodium and chlorine—nature supplies us abundantly in but the one form of this important substance. He speculates on the profound changes which will be brought about by the industrial electrolysis of salt in the other processes of chemical industry which have hitherto been connected with and dependent on the Leblanc process. He notices the fact that already electrolytic chlorine and bleaching-powder, potassium chlorate, and caustic potash have been successfully made from the potassium chloride of Stassfurt carnallite. Notice is taken of the plan adopted at Leopoldshall for making the osmotic diaphragms of parchment-paper permanent; namely, by adding on the anode side about 2 *per cent.* of cal-

cium chloride or magnesium chloride to the brine to be electrolyzed, with the effect of forming an adherent deposit of an oxychloride of calcium or magnesium on the diaphragm, which serves to protect it. Liquefied chlorine placed upon the market in steel cylinders is mentioned as one of the newer chemical products. We have a discussion of the various attempts since 1889 (the date of the French International Exposition) to recover in useful form the chlorine of salt treated by the Solvay ammonia-soda process, with, as yet, no really satisfactory solution of the problem.

Improvements in the manufacture of sulphuric acid are limited to the means of concentrating the acid. The apparatus of Scheurer-Kestner is intended to effect a partial concentration in a platinum vessel, followed by final concentration in one of cast-iron, the transfer from the one to the other being made when the strength attained begins to entail considerable attack of the platinum and the acid ceases to appreciably act on the cast-iron. An apparatus on this principle required but 18.8 kilos of platinum, the iron part weighing 250 kilos; 4500 kilos of sulphuric acid of 95 *per cent.* could be turned out in twenty-four hours, and the loss of platinum was not more than 0.15 gram per ton of acid of 66° B. The gold-coated platinum of Herœus is mentioned, with notice of the permanent and satisfactory union of the two metals brought about by casting the gold on the surface of previously heated ingots of platinum and rolling down the compound bars so produced. The interesting proposal of Blount is not overlooked, to concentrate the acid in a glass or porcelain vessel by a platinum-wire spiral heated by the passage through it of an electric current—a wire 5 mm. in diameter and 77 cm. long, heated to 480° C. by a current of 364 amperes (at 5 volts), sufficed to concentrate 24 kilos of acid in five hours—this represents a consumption of 5 times as much fuel as would be required for direct concentration, but water-power would afford a cheaper source of power, and the quantity of platinum required is very small, while any loss from electrolytic action might, it is suggested, be avoided by using alternating currents.

The great increase of production of nitric acid, as well as sulphuric acid, of high strength, is due to the demand for the manufacture of modern explosives. At Griesheim, pure and strong nitric acid is made by condensing in a receiver kept at 80° C., beyond which is a reflux condenser; the more volatile impurities, including the lower oxides of nitrogen, are carried on.

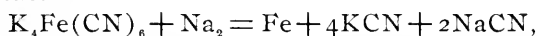
A description is given, with a figure, of the improved form of revolving iron cylinder adopted by the Solvay firm for the heating of bicarbonate of soda made by the ammonia process

in order to convert it into the normal carbonate, a regulated amount of the latter, from a previous operation, being mixed in with the new material to be treated.

The facts are quoted with interest in respect to the natural carbonate of soda held in solution by the water of Owens Lake, in Inyo County, California. Chatard's report estimating the total amount of this carbonate in the lake at 40 to 50 millions of tons—the product, so far obtained in a small way only, has the composition $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O}$, but can, of course, be converted into the normal carbonate by heating.

There is an account of Castner's new industrial product, sodium dioxide, likely to prove a valuable laboratory reagent, which is made, chiefly for use in bleaching, by the Aluminium Company (limited) of London and Oldbury—prepared by heating metallic sodium to 300°C . in vessels of aluminium, and passing over it at first air nearly deprived of oxygen, and at the end of the process air containing its full proportion of oxygen. The product is best applied in bleaching along with magnesium sulphate, so as to avoid the ill effects of the alkaline soda if unneutralized.

An interesting result is presented of the reduced demand for metallic sodium, due to aluminium being now made by electrolysis, in the application of the former metal to the manufacture of a mixed potassium and sodium cyanide (sold as "cyanide of potassium" for use in the metallurgy of gold) by the reaction.



which, unlike the older processes, avoids the formation of cyanate and utilizes the whole of the cyanogen present.

Under the head of "Produits chimiques et pharmaceutiques" are included all the finer chemicals, especially those of organic character. There is a passing remark on the difficulty in distinguishing at Chicago, in the American department, between products really made in the United States and those which American houses sent to the exhibition, although acting only as importers or agents for European firms.

The great activity shown of late years in the production of new medicinal agents, and in the investigation of their physiological effects, is commented upon, and a long list is presented of these substances, partly of natural origin, extracted from vegetable sources—new alkaloids, glucosides, etc.,—and partly prepared by synthetic laboratory methods. The enormous increase in the production of quinine, followed by a fall in price from 800 to 1,000 francs per kilogram thirty years ago to 30 or 40 francs now, is noted, and the occurrence at the Chicago exhibition of fine specimens of cupreine, the alkaloid from *Remigia pedunculata*, of which the relation to

quinine has been shown by Grimaux and Arnaud, quinine being methyl-cupreine. Sparteine, now applied to medical use, and gymnemic acid, from the leaves of *Gymnema sylvestris*, with its curious effect upon the nerves of taste, rendering them insensible to the impressions of bitter or sweet, are among the newer substances of natural origin which are mentioned. As regards chloroform, notice is taken of the now general practice of first independently preparing chloral and then decomposing it by an alkali, and also of the Pictet method of purifying chloroform by crystallizing it on exposure to very low temperature (the melting-point is -62° C.). But nothing is said as to the extensive substitution of acetone for alcohol as the prime material. Among the synthetic products for medical use are noticed diethylene-diamine (piperazine) as a solvent for uric acid, and paraphenetol-carbamide (sucrol) as a sweetening material when sugar is to be avoided.

Attention is drawn to the extension and growing importance of photographic chemicals, and of those used as reagents in scientific laboratories and in analysis. There has been marked improvement of late years in the variety of these attainable, and in the purity of condition which many of them present as they can now be purchased.

Interesting little specialties are noted in the "artificial spindle oil" exhibited by the Russian firm of Krestovnikoff Brothers, of Kasan, an oleate of amyl, and the "lipogenine" of the same firm, a palmito-stearate of ethyl. These products suggest a comparatively little trodden path, the investigation of the various esters and other salts of the higher fatty acids, artificially produced. A step in the industrial application of such work was taken a number of years ago, when the *Aktien-Gesellschaft für Anilinfabrikation* of Berlin began to make their *Anilinfettfarben* for color-printing, salts of linoleic, etc. acids with the colored triamine bases, rosaniline, etc.

The report contains an extended discussion of the structure of the principal artificial coloring materials used in modern dyeing, and of the difficult question of general relation between structure and tinctorial properties, the reporter adopting provisionally Witt's classification of these materials in 17 groups. Reference is made, for the general history of this department of chemical industry, to Caro's admirable lecture before the German Chemical Society in 1892. The exhibition of coal-tar colors was not by any means so extensive and brilliant at Chicago as at several places at which previous expositions had been held; it is noted that there were but three European firms producing these colors represented, out of about thirty such firms in existence and at work. Among the newer materials of this kind are particularly noticed—new anthracene

blues, producing very fast tints on wool, which resist exposure to air, light, and washing with soap, fully replacing indigo in wool-dyeing—indoine, a derivative of pheno-safranine, giving good results resembling those of indigo on *cotton*—and some valuable new rhodamines. There was a fine display of artificial indigotine, and of the various materials which are required for its synthesis by different lines of approach.

Under the head of materials for perfumery it is remarked that France is still, as she has long been, the leading producer of natural perfumes of vegetable origin, but that of late years the cultivation of flowers, etc., for this use has been extended from the French Mediterranean coast to that of Algeria, where there are now large plantations under exceedingly favorable conditions as respects climate. The only essential oil mentioned, as produced in the United States, is that of mint; no notice is taken of other American specialties, such as *sassafras* and *wintergreen* (*gaultheria*). There is a decided advance reported in the production of artificial or synthetic perfumes—the isolation of *irone*, as the odorous principle of the iris and the violet, and the extraction from oil of lemon of *citral*, from which (itself a substance of but moderate cost) can be produced synthetically *ionine*, isomeric with *irone*, and having the same iris and violet odor—the production of *aubepine* (anisic aldehyde), *neroline* and *yara-yara* from β -*naphthol*, etc.

The report is sent out from the "*Imprimerie Nationale*," and illustrates the clearness and elegance of French typography.

J. W. M.

The Density of Oxygen and Hydrogen; a Correction.

The scale of the barometer with which the pressures of the gases were measured in the experiments mentioned on page 274, was compared with two metres procured from the Société Genevoise, and accompanied with its statement purporting to give their true length. But both have now been compared with the Standards of the United States Coast and Geodetic Survey, with the result that the length certified by the maker is in error by 1/30000. The densities given for the gases should, therefore, be increased by 1/3000; when they become:

Density of oxygen, latitude 45°... 1.42900 \pm 0.000034

Density of hydrogen..... 0.089873 \pm 0.0000027

The correction is, of course, smaller than the remaining uncertainty of the densities; but the corrected values are the actual results of the experiments. EDWARD W. MORLEY.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

ON THE ACTION OF BENZIMIDOMETHYL ETHER ON AROMATIC ORTHO COMPOUNDS.

BY H. L. WHEELER.

This paper consists of a description of benzimidomethyl ether and of its action on orthoamidophenol, orthoamidothiophenol, orthophenylenediamine, and on orthotoluylenediamine. These reactions resulted in the formation of anhydros-bases.

Benzimidomethyl Ether.—Tafel and Enoch¹ have shown that by the action of ethyl iodide on the silver salt of benzamide, benzimidoethyl ether is formed. The benzimidomethyl ether used in these experiments was prepared in the same manner. Silver benzamide, suspended in dry ether, was treated with an excess of methyl iodide, and, after standing several days, the mixture was diluted with more ether. It was then filtered and, on evaporating off the ether on the water-bath, the benzimidomethyl ether was obtained as a light yellow colored oil. This, on cooling to -30° , did not solidify. It has a peculiar, but not unpleasant, aromatic odor. It dissolves in acids and is precipitated again by alkali or ammonia. The hydrochloric acid solution gives yellow crystalline precipitates with both gold and platinum chlorides. For analysis the

¹ Ber. d. chem. Ges., **23**, 104.

platinum-chloride precipitate was washed with dilute hydrochloric acid and dried over sulphuric acid.

0.1960 gram substance gave 0.0570 gram platinum.

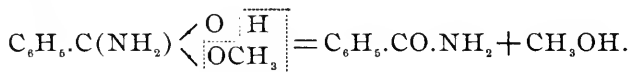
	Found.	Calculated for [C ₆ H ₅ .CCl(NH ₂)OCH ₃] ₂ .PtCl ₄ .
Pt = 195.5	29.0	28.7

For purposes of comparison benzimidomethyl ether was prepared by the action of hydrochloric acid gas on a mixture of benzonitrile and methyl alcohol, according to the method of Pinner.¹ From the hydrochloric-acid addition-product thus obtained, the free imido-ether was liberated by means of potassium carbonate. This was found to have properties identical with the above.

Benzimidomethyl ether differs from benzimidoethyl ether, its homologue, by not readily yielding cyanphenine on standing. Indeed, Pinner² states that the best method for preparing cyanphenine is to allow benzimidoethyl ether to stand.

Benzimidomethyl ether was allowed to stand exposed to the air in a beaker glass for several weeks. Colorless crystals were slowly formed. These were washed from unaltered benzimidomethyl ether with ligroïn and then crystallized from dry benzene. The product then melted below 60°. On recrystallizing from benzene it melted from 120°–125°; again recrystallized, it melted at 128°. It was readily soluble in alcohol and in ether, and crystallized from water in plates. The substance was, therefore, benzamide. It was further identified as benzamide by preparing the silver salt.

In another experiment a few drops of the imido-ether were covered with a layer of water, in which it is somewhat soluble, and the whole allowed to stand. In about a month the oil had completely changed into well-crystallized plates of benzamide. The formation of benzamide by the action of water on benzimidomethyl ether seems to be best explained by the assumption that, first, an addition of water takes place, and that the resulting compound then gives off methyl alcohol as follows:

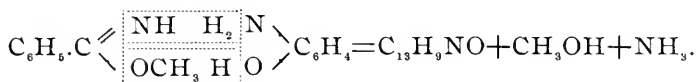


¹ Ber. d. chem. Ges., **16**, 354, 1654.

² Ber. d. chem. Ges., **22**, 1611.

Benzenylorthoamidophenol, $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$.—The investigation of the action of benzimidomethyl ether on orthoamidophenol was undertaken in order to determine whether an oxyamidine would result, *i. e.*, $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \diagup \text{NH} \\ \diagdown \text{NH} \cdot \text{C}_6\text{H}_4\text{OH} \end{smallmatrix}$.

This then, by dehydration, might lead to a phenanthridine synthesis. However, no evidence was found of the formation of such a compound. The only crystalline product obtained was benzenylorthoamidophenol, the condensation taking place according to the following:



This reaction is, therefore, similar to that observed by Sandmeyer¹ in the case of imidocarbonic ethyl ether and aromatic ortho compounds.

When orthoamidophenol and benzimidomethyl ether are mixed and warmed on the water-bath (the reaction takes place slowly, if at all, in the cold) ammonia and methyl alcohol are given off. The reaction requires only a few minutes for its completion. On cooling, the mass solidifies. Any unaltered amidophenol can be removed by shaking the ethereal solution with alkali; nothing but amidophenol was obtained from the alkaline solution. On evaporating off the ether and crystallizing the residue from dilute alcohol, the anhydro-base separates in beautiful long yellow needles. It can be obtained colorless by distilling in a current of steam, or by dissolving it in concentrated hydrochloric or sulphuric acid and diluting with water. It then separates in the form of shining plates melting at 103° . These separate from dilute alcohol in long needles. A nitrogen determination gave the following results:

0.4064 gram of substance gave 25.5 cc. N at 17.5° and 751 mm.

	Found.	Calculated for $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$.
N	7.18	7.18

¹ Ber. d. chem. Ges., 19, 2650.

No salts of this base were obtained except the platinum and gold double salts. The latter can be crystallized from alcohol containing concentrated hydrochloric acid. It then separates in the form of shining yellow needles. These are immediately decomposed by cold water. Analysis:

0.1960 gram substance gave 0.0719 gram Au.

	Found.	Calculated for $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{HCl} \cdot \text{AuCl}_3$
Au = 197.2	36.7	36.8

This base is, therefore, benzenylorthoamidophenol. Ladenburg¹ has shown that this compound was probably first obtained by Morse by the action of benzoyl chloride or orthoamidophenol hydrochloride. Ladenburg obtained it by acting on the free amidophenol with benzoyl chloride. On distilling, the fraction boiling between 314°–317° was found to contain this compound. This temperature is erroneously given in the text-books as its boiling-point. An experiment with the pure compound, using an Anschütz thermometer, showed that the compound boiled above 360°. This compound was also obtained by Hübner and Stünkel² from ortho-nitrophenyl benzoate.

Benzenylorthoamidophenol can also be obtained by distilling orthoamidophenol with benzamide. Benzamide reacts in this case, therefore, as if it had the structure $\text{C}_6\text{H}_5\text{C}(\text{OH})\text{:NH}$ analogous to the imido ether. It seems more probable though that the reaction takes place, first, with the formation of amidophenyl benzoate, since Guareschi³ has shown that benzamide reacts with phenol forming phenol benzoate, and the amidophenol benzoate thus formed, then—as Hübner and Stünkel⁴ have shown—readily loses water with the formation of the anhydro-base.

It can also be obtained by distilling orthoamidophenol with benzonitrile, by boiling with benzaldehyde, or by heating mixtures of the amidophenol and benzanilide in a sealed tube to 250° and then distilling. The crude products thus obtained dissolve in ether with a greenish-yellow fluorescence and crystallize from alcohol in yellow needles.

¹ Ber. d. chem. Ges. **9**, 1526.

² Ann. Chem. (Liebig), **208**, 290.

³ Ann. Chem. (Liebig), **171**, 140.

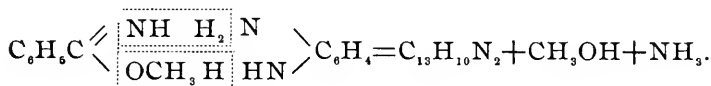
⁴ Loc. cit.

Benzenylorthoamidothiophenol, $\text{C}_6\text{H}_5\cdot\text{C} \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$.—The thiophenol necessary for this experiment was prepared from the disulphide $\begin{array}{c} \text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \\ | \\ \text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \end{array}$ by reduction with tin and hydrochloric acid, according to the directions of Hofmann.¹

2.4 grams orthoamidothiophenol and 2.6 grams benzimido-methyl ether were mixed in ethereal solution and evaporated to dryness on the water-bath without any apparent reaction taking place. On heating to 110° , ammonia and methyl alcohol were given off. When the evolution of ammonia had practically ceased, the mass was cooled. It was then dissolved in concentrated hydrochloric acid and filtered from a trace of insoluble matter. The anhydro-base was precipitated by adding water. It separated as a curdy, white mass which, by the following properties, was readily identified as benzenylorthoamidothiophenol (benzenylamidophenylmercaptan), described by Hofmann.² It melts at 114° – 115° . On crystallizing from dilute alcohol or hydrochloric acid, it separates in long, colorless needles having the odor of roses and geraniums.

Benzenylorthophenylenediamine, $\text{C}_6\text{H}_5\cdot\text{C} \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$.—

Benzimidomethyl ether reacts with orthodiamines, phenylenediamine for example, according to the following:



1.8 grams of benzimidomethyl ether and 1.2 grams of orthophenylenediamine were mixed in ethereal solution and evaporated to dryness on the water-bath. At first there was no evidence of a reaction, but on heating for a few minutes on the water-bath the reaction slowly took place. It may be hastened by warming to 115° – 120° , but then a slight decomposition of the imido ether takes place. In a short time the mass began to solidify. After the reaction was ended the product was washed with chloroform; this left the anhydro-base in the form of colorless tables which, by their high melt-

¹ Ber. d. chem. Ges., 12, 2363.

² Loc. cit.

ing-point, *i. e.*, 280° , were readily identified as benzenylorthophenylenediamine or anhydrobenzdiamidobenzene, which Hübner¹ obtained by reducing orthonitrobenzanilide. The following properties also served to identify it. The base is difficultly soluble in benzene and chloroform, also in water. It is somewhat soluble in sodium hydroxide but not in ammonia, which readily precipitates its acid solutions. It yields a difficultly soluble nitrate and sulphate. The hydrochloric acid salt was easily soluble in warm water but quite difficultly soluble in hydrochloric acid. The hydrochloric-acid solution of the base gives a yellow precipitate with gold chloride. This, on crystallizing from alcohol diluted with hydrochloric acid, separates in the form of fine long yellow needles. The crystals are readily soluble in alcohol but very difficultly soluble in water and hydrochloric acid. Analysis:

0.1375 gram substance gave 0.0503 gram Au.

	Found.	Calculated for $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{HCl} \cdot \text{AuCl}_3$.
Au = 197.2	36.5	36.8

Benzenylorthotoluylenediamine, $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CH}_3$.—

Two grams of orthotoluylenediamine ($\text{CH}_3, \text{NH}_2, \text{NH}_2$; 1,3,4.) were mixed with 2 grams of benzimidomethyl ether and heated on the water-bath. Methyl alcohol and ammonia were given off and the mass soon solidified. The product was then crystallized from dilute alcohol. It separated as a yellowish white crystalline mass melting from 238° – 240° . It was found to be identical with the compound obtained by Hübner² by the action of benzoyl chloride on benzmetamidoparatoluidine. It can be readily purified by converting it into the sulphate or hydrochloride which, as Hübner observed, are difficultly soluble in water. On adding gold chloride to the hot hydrochloric-acid solution of the base, a gold double salt is formed. This separates, on cooling, in the form of beautiful long yellow needles. These, dried over sulphuric acid, gave the following result on analysis:

0.1845 gram substance gave 0.0661 gram Au.

¹ Ann. Chem. (Liebig), 208, 302.

² Ann. Chem. (Liebig), 208, 316.

	Found.	$\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{NH} \end{smallmatrix} \text{C}_6\text{H}_3\cdot\text{CH}_3\cdot\text{HCl}\cdot\text{AuCl}_3$	Calculated for
Au = 197.2	35.8		35.9

Experiments were undertaken in order to obtain an anhydro-base from orthobromaniline and benzimidomethyl ether, without success.

ON THE ACTION OF SOME INORGANIC CYANIDES UPON CHLOROCAFFEINE.¹

BY M. GOMBERG.

CAFFEINECARBOXYLAMIDE.

In a previous paper² upon *Trimethylxanthine and Some of its Derivatives*, I have briefly described a compound obtained by the action of potassium cyanide upon chlorocaffeine. The insoluble product thus obtained did not agree with the formula of cyanocaffeine, the preparation of which was the object of the experiment. According to E. Fischer,³ prolonged boiling of bromocaffeine with a dilute alcoholic solution of potassium cyanide results in the formation of a small quantity of *amidocaffeine*. It was reasonable to suppose that the action of potassium cyanide upon chlorocaffeine would be similar to that upon the bromo-compound. But whenever chlorocaffeine was boiled under an inverted condenser with the calculated quantity of potassium cyanide in 70–80-per cent. alcohol, there always came down within one to two hours a precipitate consisting of a heavy, amorphous, slightly yellowish powder. This was filtered off, washed with hot alcohol, water, dilute hydrochloric acid, and dried at 110° C. The yield was usually from 80–85 per cent. of the weight of chlorocaffeine employed. The compound is insoluble in either hot or cold water, alcohol, chloroform, ether, or benzene; soluble in strong mineral acids. It does not melt at 360° C. The results of elementary analysis showed this compound to be neither cyanocaffeine nor amidocaffeine, as will be seen on comparing the theoretical figures with those obtained as an average of a great many determinations.

¹ From the author's thesis, presented for the degree of Doctor of Science to the Council of the Graduate School of the University of Michigan, June, 1894.

² This Journal, 14, 611.

³ Ann. Chem. (Liebig), 215, 266.

	Calculated for $C_8H_9(CN)N_4O_2$.	Calculated for $C_8H_9(NH_2)N_4O_2$.	Found.
C	49.31	33.50	45.70
H	4.12	5.30	4.83
N	31.96	33.50	29.56

The subject has since been studied more in detail, and the results of the investigation are presented in the following paper.

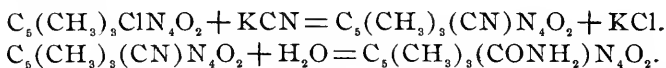
Action of Potassium Cyanide upon Bromocaffeine.—10 grams of bromocaffeine were boiled together with 3 grams of potassium cyanide in 300 cc. of 80-per cent. alcohol. Within less than two hours a heavy, amorphous precipitate separated; this was filtered off, washed with hot alcohol, dilute hydrochloric acid, and water, and finally dried at $110^\circ C$. The yield was 8 grams. In appearance and in solubility, this compound seemed to be identical with that obtained from chlorocaffeine, and this is confirmed by the elementary analysis:

- I. 0.2154 gram gave 0.3627 gram CO_2 + 0.0935 gram H_2O .
- II. 0.1644 gram gave 0.2736 gram CO_2 + 0.0720 gram H_2O .
- III. 0.1758 gram gave 44 cc. N at 14° and 754 mm.
- IV. 0.2280 gram gave 59.3 cc. N at 16° and 734 mm.
- V. 0.1755 gram gave 44.2 cc. N at 14° and 742 mm.

Calculated in percentage the results are:

	I.	II.	III.	IV.	V.	Mean.
C	45.91	45.43	45.67
H	4.83	4.86	4.85
N	29.68	29.83	29.39	29.63

It was suggested in the previous paper that the compound described above might be caffeine, in which the hydrogen of the (CH) group is replaced by the (CONH₂) group. In other words, cyanocaffeine is produced in the reaction, but is only an intermediate product; and it suffers partial saponification as soon as formed, with the production of *caffeinecarboxylamide*.



The supposition that we had here an acid-amide was based,

primarily, upon the results of the ultimate analysis, as is seen on comparing them with the theoretical figures :

	Calculated for $C_8H_9(CONH_2)N_4O_2$.	Found.
C	45.56	45.70
H	4.56	4.83
N	29.54	29.56

The second reason for assuming that we had here a partially saponified nitrile, was the probability of the reaction. The direct formation of an acid-amide from a halogen compound, through the action of potassium cyanide, is somewhat rare, but not altogether unusual. The view expressed above has since been entirely substantiated (1) by withdrawing the elements of water from caffeinecarboxylamide, and thus obtaining cyanocaffeine; (2) by estimating the amount of carbon dioxide produced when the acid-amide is heated with sulphuric acid, and (3) by the further saponification of the acid-amide to caffeinecarboxylic acid.

CYANOCAFFEINE.

Action of Phosphorus Pentoxide.—Five grams of caffeinecarboxylamide, thoroughly mixed with about an equal quantity of phosphorus pentoxide, were heated in an oil-bath at 250° C., for several hours. The mixture turned very dark and a considerable amount of tarry material was formed. The mass, on cooling, was extracted with alcohol, and the latter, when cold, gave a dark granular deposit. This was now dissolved in chloroform, and to the filtered chloroform solution ether was gradually added till the solution became turbid. In a short time there appeared a crystalline deposit, separating in small beautiful rosettes of yellow color. The yield was rather small—about 1.5 grams. The compound, dried at a gentle heat to a constant weight, was analyzed with the following results:

I. 0.1720 gram gave 0.3082 gram CO_2 + 0.0641 gram H_2O .

II. 0.1825 gram gave 52.8 cc. N at 20° and 730 mm.

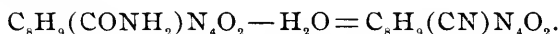
Another sample, prepared more carefully and having only a slight yellow tint, furnished these figures:

III. 0.2912 gram gave 0.5262 gram CO_2 + 0.1099 gram H_2O .

IV. 0.2408 gram gave 69.6 cc. N at 28° and 743 mm.

	Calculated for $C_8H_9(CN)H_4O_2$.	I.	II.	Found	III.	IV.
C	49.31	48.87		49.34
H	4.12	4.13		4.19
N	31.96	32.52		32.19

The effect of the phosphorus pentoxide is, of course, the removal of one molecule of water from a molecule of caffeine-carboxylamide,



It was found by repeated experiments that it is not necessary to heat the mixture above 180°–200° C. Moreover, if the fusion is allowed to go on quietly, without any stirring, for about twenty minutes before completing the experiment, the mixture will separate into two layers: an upper spongy, dark layer of phosphoric acid, and a pale-yellow, compact mass of cyanocaffeine at the bottom of the tube. The cyanocaffeine can thus, at once, be separated from the phosphoric acid mechanically in very pure condition.

Cyanocaffeine can be obtained perfectly white by repeatedly dissolving it in chloroform and precipitating with ether; also by recrystallization from hot alcohol. When obtained by either of the above processes, or by sublimation, it consists of small prismatic crystals, belonging, probably, to the triclinic system, and peculiarly arranged in clusters. It melts at 151° C., and does not congeal till the temperature sinks to 109°–110°. It sublimes without decomposition at about 160°. The compound is soluble in hot water, hot alcohol, dilute or strong; soluble in methyl alcohol, very soluble in chloroform, more soluble in hot benzene than in cold, insoluble in ether.

The behavior of cyanocaffeine towards water and dilute alcohol is worthy of notice. In the action of potassium cyanide upon chlorocaffeine in dilute alcohol, the formation of caffeine-carboxylamide was explained by the assumed instability of the cyano-compound and its great tendency towards assimilation of water. When, however, cyanocaffeine, prepared by dehydration of the acid-amide, is dissolved in boiling water, or in boiling dilute (50–70-per cent.) alcohol, it does not show any such great tendency towards hydration. When boiled with water, it changes into the insoluble acid-

amide, but not until after about thirty to sixty minutes' boiling, while with dilute alcohol the cyanocaffeine can be boiled for over an hour without any saponification into the acid-amide. But when to the hot solution of the cyano-compound in either water or dilute alcohol, a fragment of potassium cyanide is added, there appears, within two to three minutes, a precipitate of the insoluble acid-amide. The change is rapid and complete. The chlorides of potassium and sodium do not seem to bring about the hydration in the same manner as the potassium cyanide does. Nor has the latter the same effect at all when methyl alcohol is substituted for ethyl alcohol. When strong ethyl alcohol (97-98-per cent.) is used as a solvent for cyanocaffeine, the solution can be boiled* for hours, with or without the addition of potassium cyanide, and no hydration takes place. The same is true of methyl alcohol, even when only 75-80-per cent. strong.

This influence of potassium cyanide upon cyanocaffeine offers a satisfactory explanation, why caffeine-carboxylamide and not cyanocaffeine is formed, when chlorocaffeine is acted upon by a solution of potassium cyanide in dilute alcohol.

The preparation of cyanocaffeine by a direct method was then undertaken by using different cyanides and varying the nature of the solvents.

Action of Potassium Cyanide upon Chlorocaffeine in Absolute Alcohol.—Henry¹ has called attention to the fact that the interchange of the cyanogen group for the halogen atom takes place usually when the alcohol is dilute. This would be especially true when the operation is conducted at ordinary atmospheric pressure, since potassium cyanide is almost insoluble in absolute alcohol. In this instance, there was no action whatever when chlorocaffeine and potassium cyanide in absolute alcohol were boiled under an inverted condenser for several days. Chlorocaffeine was next mixed with a little more than the calculated quantity of potassium cyanide in absolute alcohol, and the sealed tube heated at 100° for fifteen hours. The alcohol was then driven off on the water-bath and the residue digested with chloroform, in which both chlorocaffeine and cyanocaffeine are easily soluble. To the fil-

¹ Compt. rend., 104, 1181.

tered chloroform solution ether was gradually added. The white precipitate which came down at this stage was entirely unlike the definitely crystalline form of cyanocaffeine. It melted sharp at 187° , the melting-point of chlorocaffeine being 188° . In appearance and behavior, as well as in the percentage of chlorine it contained, the substance was identified as pure unchanged chlorocaffeine.

Samples were then heated at 150° – 160° for about five hours. The resulting product was of a dark greenish color, extremely difficult of purification. It was found to consist, for the most part, of unchanged chlorocaffeine, some caffeinecarboxylamide, and, perhaps, a small quantity of cyanocaffeine. The only indication that the latter was present, was furnished by a small crop of crystals obtained by fractional precipitation, which melted considerably lower than chlorocaffeine and a little higher than cyanocaffeine.

Action of Potassium Cyanide in Water.—When chlorocaffeine was heated with the calculated quantity of potassium cyanide, or with an excess of it, in water, there was apparently no reaction to speak of, even when the boiling was continued for three days. The large, bulky mass which separated on cooling was found to contain a small quantity of caffeinecarboxylamide, the rest being pure unchanged chlorocaffeine, as was shown by the melting-point and the percentage of chlorine.

Action of Potassium Cyanide in Methyl Alcohol.—Potassium cyanide appears to be more soluble in methyl alcohol, both dilute and strong, than in ethyl alcohol. Calculated quantities of chlorocaffeine and potassium cyanide in about 90-per cent. methyl alcohol, were boiled under an inverted condenser for several hours. The residue, after evaporation of the alcohol, was considerably colored, the green color usually increasing in depth with the dilution of the alcohol and the length of boiling. The mixture was treated and examined, as described under ethyl alcohol, and showed, beyond any doubt, the presence of some cyanocaffeine. The melting-point varied in different samples from 145° – 160° , but ultimate analysis showed that in no case did the amount of cyanocaffeine exceed 20 per cent., the rest being chlorocaffeine. All efforts to sepa-

rate these two compounds were unsuccessful, since chlorocaffeine and cyanocaffeine resemble each other so closely in their solubility in water, alcohol, chloroform, etc. Diluting the alcohol to 50–70 per cent. did not give any better yield. In all instances the formation of the acid-amide was only very slight or none at all.

When absolute methyl alcohol was substituted for the dilute alcohol, the results were practically the same, the products being purer. Samples were then heated with absolute alcohol in sealed tubes at 100°. The contents became highly colored, even at the end of two hours. They were found to contain large quantities of unchanged chlorocaffeine, some caffeinocarboxylamide, and a small quantity of the cyanocompound.

Action of Mercuric Cyanide.—Heating chlorocaffeine with mercuric cyanide in alcohol for several days, under an inverted condenser, gave no indication of the formation of either cyanocaffeine or the acid-amide. When the heating was conducted under pressure, at 150°–200° for twenty hours, a small quantity of the acid-amide was formed, and a little separation of metallic mercury took place; otherwise the chlorocaffeine remained white and unchanged.

Action of Potassium Mercuric Cyanide.—It was very surprising to find that the double salt had no action upon chlorocaffeine. The experiments were made by using both dilute and strong ethyl alcohol,¹ methyl alcohol, and water. The heating was conducted under inverted condensers and in sealed tubes, at temperatures varying from 100°–200°, but beyond the separation of some metallic mercury and the formation of a small quantity of the acid-amide, the analysis showed that the chlorocaffeine was not attacked.

Action of Potassium Cyanide upon Fused Chlorocaffeine.—Chlorocaffeine was thoroughly mixed with finely powdered potassium cyanide, placed in a test-tube and heated in a sulphuric-acid bath, the temperature being determined by a thermometer in the tube. At about 200° the chlorocaffeine was all melted. The mixture was kept at that temperature for

¹ The double salt potassium mercuric cyanide is insoluble in strong alcohol, both methyl and ethyl.

about five hours, with frequent stirring, as the potassium cyanide and chloride settle to the bottom. The dark yellow mass, when cold, was extracted with chloroform, ether added to the filtered solution, and the precipitated mixture of chlorocaffeine and cyanocaffeine was purified by recrystallization from methyl alcohol. The product melted at 144° , and looked not unlike cyanocaffeine. But an estimation of chlorine and nitrogen showed that the mixture contained only about 30 per cent. of cyanocaffeine and 70 per cent. of chlorocaffeine. Here again all efforts to separate the two compounds completely, proved fruitless. In one instance, when the fusion was continued for fifty hours, the cyanocaffeine constituted about 60 per cent. of the mixture, but the product was very dark.

It would appear, from what has been said above, that the best method of preparing pure cyanocaffeine is by the dehydration of caffeine-carboxylamide by means of phosphorus pentoxide. Of the direct methods, the one of fusing chlorocaffeine with potassium cyanide, promises the best results; next to that, that of treating chlorocaffeine with potassium cyanide in methyl alcohol.

In concluding the description of the work upon cyanocaffeine, one more experiment, of an entirely different nature, may be mentioned: 2 grams of cyanocaffeine were dissolved in hot absolute amyl alcohol (B. P., 129° – 131°) and to the boiling solution twice the calculated quantity of metallic sodium was added. The alcohol was removed by distilling, water added, the solution slightly acidulated with hydrochloric acid, and evaporated to dryness. The residue was exhausted with absolute ethyl alcohol. This, on concentrating, deposited a thick, brown, tarry mass, in which after two days standing, there appeared long, well-defined crystals imbedded in the dark mass. These crystals could not be freed entirely from the resinous material by water, alcohol, chloroform, or ether. It was shown to be a hydrochloride of an organic base. Unfortunately the substance could not be obtained of sufficient purity to allow a complete analysis. But from its ready union with acids to form salts, its separation by alkalies, and its murexide-test, there is good reason to

think that the compound was most probably *caffeylmethylamine*, $C_8H_9N_4O_2(CH_2NH_2)$, formed by the reduction of the cyanide: $C_8H_9(CN)N_4O_2 + 4H = C_8H_9(CH_2NH_2)N_4O_2$.

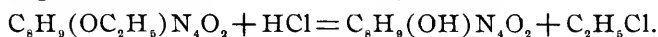
SAPONIFICATION OF CAFFEINECARBOXYLAMIDE.

Hydroxycaffeine.—In preparing larger quantities of caffeine-carboxylamide by the method above described, the alcoholic filtrate from the insoluble acid-amide was in some instances concentrated, acidulated with hydrochloric acid, and evaporated to dryness. The residue was extracted with hot absolute alcohol. When cold, the alcohol gave a deposit of long white silky needles. These, when washed and dried, were found to be of a decidedly acid reaction, melting above 300° ; insoluble in cold, but soluble in hot water. It was first taken for caffeine-carboxylic acid, $C_8H_9(COOH)N_4O_2$, but ultimate analysis showed that it was not that:

- I. 0.0686 gram gave 0.1153 gram CO_2 + 0.0330 gram H_2O .
 II. 0.2065 gram gave 50 cc. N at 22° and 746 mm.

	Calculated for $C_8H_9(OH)N_4O_2$.	I.	Found.	II.
C	45.71	45.83	
H	4.76	5.33	
N	26.66		26.65

Hydroxycaffeine was first obtained by E. Fischer¹ by heating bromocaffeine with alcoholic potash, and treating the resulting ethoxycaffeine with dilute hydrochloric acid.

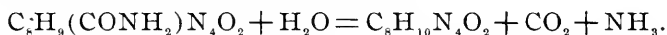


The formation of hydroxycaffeine in connection with caffeine-carboxylamide can be accounted for in two ways: (1) potassium cyanide in itself may have induced the formation of ethoxycaffeine to some extent, and this, when treated with hydrochloric acid as above described, furnished hydroxycaffeine; (2) or, during concentration of the mother-liquor some of the potassium cyanide was changed into potassium carbonate; the latter acting upon the chlorocaffeine in solution, would tend to give ethoxycaffeine, which again would furnish hydroxycaffeine when evaporated with hydrochloric acid.

Decomposition by alkalis and acids.—Repeated trials with alcoholic potash or strong hydrochloric acid as saponifying

¹ *Loc. cit.*, 215, 268.

agents, whether in open flasks or in sealed tubes at 100° – 130° , have given only negative results. When potash was employed the compound often suffered complete decomposition into methylamine, ammonia, etc. The action of hydrochloric acid was variable, depending upon the temperature. On prolonged boiling in an open flask, or more rapidly at 120° in sealed tubes, the acid-amide was converted into caffeine with simultaneous formation of carbon dioxide.



At 160° – 170° the caffeine in its turn suffered complete decomposition.¹ When the acid-amide was suspended in boiling absolute alcohol, and through the solution a stream of dry hydrochloric acid passed for many hours, there was no change whatever.

Estimation of the carbon dioxide liberated.—The acid-amide dissolves readily in concentrated sulphuric acid, also in dilute acid (1:1). On addition of water to the acid solution, the acid-amide separates out as a white amorphous powder, unchanged in composition; this is the best method for purifying caffeinecarboxylamide. But when the solution of the acid-amide in sulphuric acid (1:1) is heated on the the water-bath for about one-half hour, the whole of the caffeinecarboxylamide is converted into caffeine and carbon dioxide, according to the equation given above. Quantitative estimations of the amount of carbon dioxide thus set free were made, and the results fully confirmed the view expressed in the equation. The liberation of the gas begins at a little below 100° , but in order to gain time the temperature was raised to 130° .

I. 1.2810 grams gave 0.2411 gram CO_2 .

II. 1.3065 grams gave 0.2372 gram CO_2 .

Calculated.		Found.	
		I.	II.
CO_2	18.57	18.82	18.16

Caffeinecarboxylic Acid, $\text{C}_8\text{H}_9(\text{COOH})\text{N}_4\text{O}_2$.—A solution of the acid-amide in sulphuric acid (1:1) was gently warmed at 75° – 80° for a short time, and then water rapidly added to the acid; there soon came down a precipitate which consisted, as was found afterwards, of amorphous, unchanged acid-amide—with crystalline caffeinecarboxylic acid—and of caffeine. The

¹ E. Schmidt: Ann. Chem. (Liebig), 217, 278.

precipitate, freed from sulphuric acid by filtration and washing, was treated with cold dilute alkali, which dissolved the caffeinocarboxylic acid and any remaining caffeine, leaving behind the caffeinocarboxylamide. On adding hydrochloric acid to the alkaline solution, there came down a copious precipitate of needle-like crystals. These were filtered off, washed with cold water and alcohol, and dried. They were analyzed with the following results:

- I. 0.2794 gram gave 0.4667 gram CO_2 + 0.1094 gram H_2O .
- II. 0.2612 gram gave 0.4390 gram CO_2 + 0.1035 gram H_2O .
- III. 0.2531 gram gave 52.7 cc. N at 18° and 739 mm.
- IV. 0.1530 gram gave 33 cc. N at 21° and 734 mm.
- V. 0.1089 gram gave 22.8 cc. N at 18° and 740 mm.

	Calculated for $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{COOH}$.	I.	II.	Found. III.	IV.	V.
C	45.38	45.56	45.88
H	4.20	4.35	4.40
N	23.53	23.88	24.22	24.05

Caffeinocarboxylic acid, when pure, has the following properties: White, silky, acicular crystals of sour taste, with a bitter aftertaste; melts at 225° – 226° , with decomposition into caffeine and carbon dioxide; is of decidedly acid reaction, neutralizing alkalis and decomposing carbonates. It is insoluble in cold water and alcohol; soluble in these solvents when hot, with partial decomposition; insoluble in chloroform (unlike most caffeine compounds), carbon disulphide, and benzene; soluble in cold concentrated mineral acids without decomposition. It is an unstable acid, splitting off carbon dioxide with great facility when boiled with water or with dilute acids, or when heated by itself.

1.0234 grams of the acid, heated with dilute sulphuric acid, gave 0.1832 gram CO_2 = 17.90 per cent. 0.5198 gram, heated by itself to 150° , gave 0.0874 gram CO_2 = 16.83 per cent.,—the theoretical quantity being 18.57 per cent.

Methods of preparation.—The preparation of caffeinocarboxylic acid by the use of sulphuric acid is rather unsatisfactory, because of the small yield. In order to saponify all the acid-amide, the digestion has to be continued for some time, and the longer the digestion the more of the acid is likely to be

decomposed. Of the many methods tried, only a few need to be mentioned:

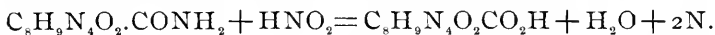
Nitric acid acts too violently, decomposing a considerable quantity of the carboxylic acid.

When the acid-amide is suspended in water, the calculated quantities of sulphuric acid and potassium nitrite added, and the flask set aside for days, there is no action whatever.

When the acid-amide is dissolved in sulphuric acid (50 per cent.) and to the cooled solution silver nitrate gradually added, there separates, on addition of water, a mixture of caffeine-carboxylic acid and a variable proportion of its silver salt. It is difficult to separate the free acid from the silver salt without considerable loss of the former.

When the acid-amide is dissolved in strong hydrochloric acid, in sulphuric acid of 50 per cent., or in sulphuric acid of 90 per cent., and set aside for two months, there is very little saponification. At the end of six months all the acid-amide was found to have disappeared and a fair yield of caffeine-carboxylic acid was obtained.

The method that proved most serviceable, however, was that based upon the use of nitrogen trioxide: The acid-amide is dissolved in sulphuric acid (1:1) and a stream of nitrogen trioxide is passed into the solution, till a few drops of the latter removed to a test-tube do not give any *amorphous precipitate* immediately on the addition of a little water, but a perfectly *crystalline* precipitate after a minute or two. When this stage has been reached, saponification is complete;



The sulphuric acid is now largely diluted with water and set aside for complete precipitation. Caffeine-carboxylic acid, thus obtained, is white and pure, the yield being usually 85-90 per cent. of the theoretical quantity.

SALTS OF CAFFEINECARBOXYLIC ACID.

Caffeine-carboxylic acid, unstable in itself, readily forms salts of considerable stability. These salts are characterized by definite crystalline structure, and are obtained in the pure state without difficulty.

Sodium caffeine-carboxylate, $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2\text{Na}\cdot 2\text{H}_2\text{O}$.—This

salt is prepared by adding sodium carbonate to a warm solution of the acid in water, evaporating to dryness, and extracting the residue with hot alcohol. On cooling, the salt separates out in fine white acicular crystals. It can also be prepared by neutralizing a solution of the acid with sodium hydride (freshly prepared from the metal) and precipitating the salt with alcohol. The composition of the salt seems to be the same in both cases. It was dried between drying papers and analyzed with the following results :

I. 0.3487 gram gave on evaporation and ignition with sulphuric acid, 0.0826 gram Na_2SO_4 .

II. 0.4128 gram gave 0.0965 gram Na_2SO_4 .

Calculated for $\text{C}_8\text{H}_9\text{N}_2\text{O}_2.\text{CO}_2\text{Na}.2\text{H}_2\text{O}$.		Found.	
Na		I.	II.
	7.77	7.68	7.58

The salt does not easily lose its water of crystallization ; 0.5935 gram having lost only 0.0015 gram when heated in a water-bath for 2 hours. At 130° the loss is quite appreciable, and the water is completely driven off at 165° .

0.5933 gram salt lost at 165° 0.0769 gram water, and gave 0.1368 gram Na_2SO_4 .

	Calculated.	Found.
H_2O	12.16	12.96
Na	7.77	7.47

The salt is very easily soluble in water and is soluble in hot alcohol. It is transposed by all mineral acids and also by acetic acid. On the addition of silver nitrate it gives a white gelatinous precipitate ; when copper sulphate is added it gives a beautiful pale-green crystalline precipitate of copper caffeine-carboxylate ; with ferric chloride it gives a dark red precipitate of a basic ferric salt.

Potassium salt, $\text{C}_8\text{H}_9\text{N}_4\text{O}_2.\text{CO}_2\text{K}.2\text{H}_2\text{O}$.—This salt is prepared in a manner similar to that of the sodium salt, which it resembles in appearance and behavior. It however loses its water of crystallization more readily than the sodium salt. The loss is appreciable when the substance is dried over sulphuric acid, and the salt thus becomes anhydrous in about two weeks. Most of the water is driven off at 100° , and all of it quite readily at 130° .

An air-dried sample was analyzed and furnished the following figures :

I. 0.4352 gram salt lost at 140° 0.0552 gram H_2O and gave 0.1187 K_2SO_4 .

II. 0.6918 gram salt lost at 170° 0.0875 gram H_2O and gave 0.1897 gram K_2SO_4 .

	Calculated for $C_8H_9N_4O_2.CO_2K.2H_2O$.	I.	Found. II.
H_2O	11.54	12.69	12.65
K	12.50	12.25	12.31

Calcium salt, $(C_8H_9N_4O_2.CO_2)_2Ca.5H_2O$.—The calcium salt was prepared by adding calcium carbonate to a warm solution of the acid, digesting on the water-bath and filtering off the excess of calcium carbonate while hot. On cooling, the calcium salt separates in long fine hair-like crystals, which grow rapidly and soon fill the beaker with a thick jelly-like mass. This was filtered and dried at a gentle heat to a constant weight. The salt does not lose in weight when heated for two hours in a steam-oven; the water of crystallization is driven off rapidly at 160° and completely at 170° . When subjected to analysis it yielded the following results :

I. 0.1719 gram salt dried over sulphuric acid to constant weight gave 0.0380 gram $CaSO_4$.

II. 0.4995 gram salt lost at 180° 0.0775 gram H_2O , and gave 0.1080 gram $CaSO_4$.

	Calculated for $(C_8H_9N_4O_2.CO_2)_2Ca.5H_2O$.	I.	Found. II.
H_2O	14.90	...	15.52
Ca	6.62	6.50	6.35

The salt is stable; does not break down at 200° . It is soluble in hot water, somewhat soluble in hot alcohol. It is decomposed by mineral acids.

Barium salt, $(C_8H_9N_4O_2.CO_2)_2Ba.5H_2O$.—The barium salt is prepared in a manner analogous to that of the calcium salt, or, by dissolving the acid in a warm solution of barium hydroxide, removing the excess of the latter with carbon dioxide, and concentrating the filtrate to crystallization. The salt separates readily in clusters of thick short acicular crystals, having the composition indicated above. The salt was analyzed with the following results :

I. 0.2535 gram salt dried over sulphuric acid to a constant weight, gave 0.0858 gram BaSO_4 .

II. 0.4820 gram salt lost at 150° 0.0615 gram H_2O , and gave 0.1620 gram BaSO_4 .

	Calculated for $(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2)_2\text{Ba}\cdot 4\text{H}_2\text{O}$	I.	Found.	II.
H_2O	12.84		12.74
Ba	19.52	19.90		19.75

Barium caffeinecarboxylate resembles the calcium salt very much, but it is less soluble in water, and still less in alcohol. It loses about 30 per cent. of its water of crystallization when heated in a steam-oven for several hours, and the remaining water is easily driven off at 150° .

Copper salt, $(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2)_2\text{Cu}\cdot 4\text{H}_2\text{O}$.—When a solution of either potassium or sodium caffeinecarboxylate is added to a solution of copper sulphate, there comes down in a minute or two a precipitate of small, beautiful, glistening crystals. The salt was washed with water, alcohol, and ether, and dried at a gentle heat to a constant weight. The analysis of this salt gave these results:

I. 0.2992 gram salt gave 0.0381 CuO .

II. 0.5230 gram salt lost at 150° 0.0627 gram H_2O , and gave 0.0655 gram CuO .

	Calculated for $(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2)_2\text{Cu}\cdot 4\text{H}_2\text{O}$.	I.	Found.	II.
H_2O	11.82		11.99
Cu	10.39	10.19		10.02

The copper salt is of a pale green color, becoming emerald-green with loss of water. It is insoluble in either hot or cold water, or alcohol. It is soluble in dilute mineral acids and in acetic acid with decomposition.

Silver salt, $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2\text{Ag}$.—When a solution of silver nitrate is added to a solution of caffeinecarboxylic acid, or to any of its soluble salts, a heavy gelatinous precipitate is at once thrown down, with almost quantitative precipitation of the silver. This precipitate, after careful washing and drying, was analyzed with the following results:

0.3258 gram gave 0.1052 gram Ag .

	Calculated for $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2\text{Ag}$.	Found.
Ag	31.24	32.02

A much better method of preparing this salt is to add an ammoniacal solution of silver nitrate to a solution of caffeine-carboxylic acid in ammonia. On driving off the excess of ammonia, the silver salt comes down in a very pure crystalline form, easily washed and dried. When analyzed it furnished the following figures:

I. 0.2442 gram gave 0.2750 gram CO_2 + 0.0751 gram H_2O .

II. 0.1882 gram gave 28 cc. N at 24° and 741 mm.

III. 0.2943 gram gave 0.0923 gram Ag.

	Calculated for $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2\text{Ag}$.	I.	Found. II.	III.
C	31.33	30.71
H	2.61	3.07
N	16.25	16.75
Ag	31.24	31.35

The silver salt is quite stable, is not transposed by comparatively strong nitric or sulphuric acid. When dry, it does not darken on exposure to sunlight for months. It is insoluble in either hot or cold water. Heated to 180° – 200° it begins to sublime slowly, and at 270° , quite rapidly. The sublimate, however, contains no silver.¹

ESTERS OF CAFFEINECARBOXYLIC ACID.

Methyl Ester, $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2\text{CH}_3$.—When silver caffeine-carboxylate is heated with the calculated quantity of methyl iodide in alcohol, at 100° or even on the water-bath with an inverted condenser, there soon separates the heavy silver iodide. The alcohol, filtered from the insoluble iodide, gives on cooling, a copious crystalline deposit of the methyl ester. This was purified by recrystallization from hot alcohol, dried to a constant weight, and analyzed with the following results:

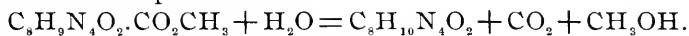
I. 0.2014 gram gave 0.3555 gram CO_2 + 0.0965 gram H_2O .

II. 0.2577 gram gave 52.6 cc. N at 23° and 735 mm.

	Calculated for $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}_2\text{CH}_3$.	I.	Found. II.
C	47.62	48.14
H	4.76	5.32
N	22.22	22.88

¹ A pure sample of the silver salt was washed with hot water to remove any remaining caffeine-carboxylic acid. It was then dried and washed with chloroform to free it entirely from caffeine. When carefully heated to 180° – 200° it gave a sublimate of beautiful white, silky crystals, melting at 227° (M. P. of caffeine = 230°), and neutral in reaction. It is difficult to conceive how caffeine could be formed by the treatment above described. The compound which sublimed is not unlikely *dicafeylketone*, $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\cdot\text{CO}\cdot\text{C}_8\text{H}_9\text{N}_4\text{O}_2$.

The methyl ester is soluble in hot water with partial decomposition; is slightly soluble in cold alcohol, more readily in hot alcohol; easily soluble in chloroform; soluble in benzene; almost insoluble in ether. It begins to sublime undecomposed, without previously melting, at about 160° ; melts sharp at 201.5° (uncorr). It does not break down when heated to above 200° , but is readily decomposed on boiling with dilute sulphuric acid:



Ethyl Ester, $\text{C}_8\text{H}_9\text{N}_4\text{O}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5$.—This ester is prepared in exactly the same way as the corresponding methyl salt, which it closely resembles in appearance. Prepared and purified as described under methyl ester, it gave, on analysis, the following figures:

0.1768 gram gave 0.3272 gram CO_2 + 0.0854 gram H_2O .

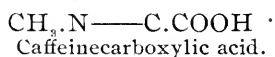
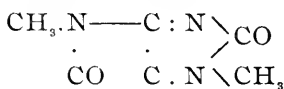
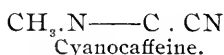
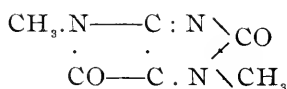
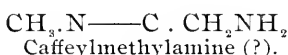
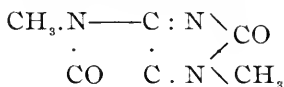
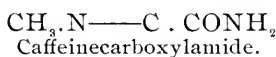
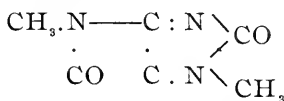
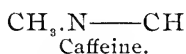
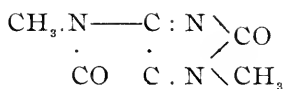
	Calculated for $\text{C}_8\text{H}_9\text{N}_4\text{O}_2 \cdot \text{CO}_2\text{C}_2\text{H}_5$.	Found.
C	49.62	50.46
H	5.26	5.36

The ethyl ester is soluble in the different solvents to about the same extent as the methyl salt. It sublimes undecomposed at about 160° and melts at 207° – 208° . Like the methyl ester it is not decomposed when heated to a temperature above 200° , but is readily decomposed when heated with dilute acids.

Attempts to prepare the corresponding *phenyl* ester proved unsuccessful. The silver salt was heated with brombenzene dissolved in benzene at 170° for several hours, but showed no change. Samples were then heated with iodobenzene at 200° for about fifteen hours. The contents of the tube were found to contain a great deal of unchanged silver caffeine-carboxylate and some silver oxide. There was also separated a small crop of crystals containing no silver. An estimation of nitrogen showed that it was not the phenyl ester. This body resembled very much the crystals obtained by the sublimation of the silver salt (p. 418).

SUMMARY.

All the new compounds described in this paper present the interesting feature, that they are the first compounds of caffeine in which the carbon of the CH group has been linked directly to a new carbon atom.



The preparation of these compounds was not undertaken with any view to either confirm or disprove the accepted structural formula of caffeine. But, as far as they go, the properties of these compounds are explained by E. Fischer's formula of caffeine quite satisfactorily.

In a previous paper¹ attention was called to the difficulty of converting bromocaffeine and chlorocaffeine into the corresponding iodo-compound by the usual treatment with the iodides of potassium, sodium, and calcium. This pointed to the tertiary nature of the CH group. The experience with mercuric cyanide and the double cyanide of mercury and potassium suggests the same view.

The instability of the carboxylic acid, and the comparative stability of its esters, is an interesting feature of this compound. This fact is in accord with the general nature of many acids in which the carboxyl is linked to an unsaturated carbon atom $\left(\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C} \cdot \text{CO}_2\text{H} \right)$. A large number of such acids split off carbon dioxide more or less readily on heating. The close proximity of the nitrogen atom will also tend to make this an unstable acid $\left(\begin{array}{c} \text{N} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \parallel \end{array} \right)$, as is the case with some amido-acids.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XII.—CAMPHORIC ACID.

THIRD PAPER.

BY W. A. NOYES.

In my last paper¹ it was shown that di-hydroamino-campholytic acid yields campholytic acid when treated with nitrous acid. A further study of the reaction has shown that there is also formed, at the same time, a hydroxy acid which evidently contains the hydroxyl group in the same position as the amino group of the acid from which it is derived. This acid possesses quite unusual interest, since, in conjunction with other compounds and relations which will be discussed in this paper, it furnishes quite conclusive proof that the carboxyl groups of camphoric acid are combined with adjacent carbon atoms. Two distinct lines of proof lead to this conclusion. One was first pointed out by Walker² and depends on the conduct of the di-bromide of campholytic acid, which indicates that the double union in that acid is in the $\alpha\beta$ position. This conclusion has received a further confirmation by a study of the conduct of campholytic acid toward dilute sulphuric acid. Fittig has shown³ that dilute sulphuric acid converts $\beta\gamma$ acids into the corresponding lactones while $\alpha\beta$ acids are not affected. Dilute sulphuric acid changes campholytic acid, it is true, *but does not convert it into a lactone*. It may be objected that the reactions which Fittig has established for unsaturated acids with an open chain do not necessarily hold good for cyclic compounds, but it will be shown in this paper that the reaction in question does convert an isomeric acid into a lactone.

The second proof that camphoric acid contains the two carboxyls combined with adjacent carbon atoms consists in the fact that the hydroxy acid which has been referred to cannot be converted into a lactone by the action of dilute acids. At least four lactones derived from camphoric acid are known; the campholactone of Fittig and Woring⁴, an isomeric lac-

¹ This Journal, 16, 505.² J. Chem. Soc., 63, 510 (1893).³ Ber. d. chem. Ges., 27, 2667.⁴ Ann. Chem. (Liebig), 227, 10.

tone to be described in this paper, camphanic acid¹, and a brom-lactone mentioned by Aschan². This shows that the presence of the ring does not interfere with the formation of lactones and furnishes almost positive proof that the hydroxyl of the hydroxy acid which I have obtained is not in the γ position with regard to the carboxyl. The only other relations possible in a pentamethylene or hexamethylene ring are the α , β , and δ positions for the hydroxyl. The δ position is inconsistent with the formation of camphoric anhydride and the α position does not agree with the differences observed in the decompositions of the two amino acids, to mention only one of many facts which could be brought forward against it. The main argument in favor of the γ position rests on the formation of camphanic acid and campholactone from brom-camphoric anhydride. But this compound loses hydrobromic acid readily,³ giving an unsaturated acid which must have the double union in the $\beta \gamma$ position, if the reasoning given above is correct, and such an acid would then give, by rearrangement, a lactone in accordance with the reaction so often observed by Fittig and his co-workers.

If the conclusion which I have reached is accepted, the formula proposed by Bredt⁴ for camphoric acid must be considered as definitely disproved. That the conduct of campholytic acid is not consistent with the tetramethylene formula of Ballo⁵ was pointed out by Walker.⁶

When campholytic acid is allowed to stand with dilute sulphuric acid for some time it is converted quantitatively into an isomeric, solid acid. Di-hydro-hydroxy-campholytic acid is converted, even more easily, into the same acid by the action of dilute sulphuric acid, but it may be converted, in part, at least, into the first campholytic by conversion into a hydrobromide and by treating the latter with caustic soda. The transformation of the campholytic acid may also be effected by means of hydrobromic acid, but less readily. The new acid has been already described by Walker⁷ under the name of camphothetic acid and was considered by him as having the composition

¹ *Ibid*, **172**, 151.

³ Aschan : *Ber. d. chem. Ges.*, **27**, 3506.

⁵ *Ibid*, **14**, 337.

² *Ber. d. chem. Ges.*, **27**, 3505.

⁴ *Ber. d. chem. Ges.*, **26**, 3049.

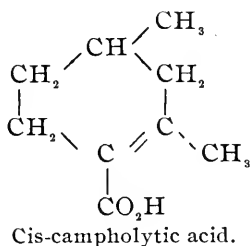
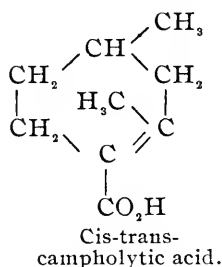
⁶ *Loc. cit.*

⁷ *J. Chem. Soc.*, **63**, 504 (1893).

$$\begin{array}{c} \text{C}_8\text{H}_{14}\text{CO}_2\text{H} \\ | \\ \text{C}_8\text{H}_{14}\text{CO}_2\text{H} \end{array}$$
 Dr. Walker has very kindly sent me a small specimen of his acid, and its conduct toward permanganate, crystalline form, and melting-point, leave no doubt that the acids are identical. The proofs for the formula $\text{C}_8\text{H}_{14}\text{CO}_2\text{H}$ will be given below.

The facts that the new acid is formed directly from dihydro-hydroxy-campholytic acid and that it is not converted into a lactone by dilute sulphuric acid compel us to the conclusion that the double union in the acid is in the $\alpha \beta$, or Δ^1 position. But the double union in the first campholytic acid is also in the Δ^1 position.

These relations can, I think, be satisfactorily explained by the following formulæ.



The configuration represented by the second formula would undoubtedly be the more stable and this is assigned to the new acid. The cis-trans formula here given has been discussed for a similar case by Baeyer¹ and has been dismissed as improbable because of the tension within the molecule to which it would give rise. If the formula is followed by means of models, however, it will be seen that there is a position in which the carboxyl and methyl groups are outside of the plane of the ring which gives rise to less tension than is found in a tetramethylene ring.

It may be objected to the formulæ given that the double union in the two acids might be in the Δ^1 and Δ^6 positions respectively. But this would be inconsistent with the fact that in the addition of hydrobromic acid the bromine appears

¹ Ann. d. Chem. (Liebig), **258**, 156.

always to take the β position.¹ Since the Δ^6 compound could only be formed from a bromine derivative having the bromine in the α position.

It has been assumed in several recent discussions of unsaturated cyclic compounds that stereoisomerism is impossible for the Δ^1 position. I believe, however, that there is already one case on record where there is an indication of such isomerism. In the study of Δ^1 tetrahydro-benzoic acid Aschan² observed a solid and a liquid acid which apparently bore to each other a relation very similar to that observed in the case of the campholytic acids. On account of the importance of the question, it is intended to examine the case more fully and it is hoped that further proof in support of these formulæ may be obtained. Meanwhile I believe that the dogma with regard to the stereoisomerism of Δ^1 compounds should be used with some caution.

By the use of models it becomes evident at once that the cis-trans-campholytic acid would give a hydrobromide in which the bromine and carboxyl are in the "cis" position. Since, as will be shown, the di-hydro-hydroxycampholytic acid gives the same hydrobromide, it follows that this is a "cis" compound and further that ordinary camphoric acid itself is a "cis" compound. This conclusion was reached some time ago by Aschan.³

In this discussion it is not intended to imply that the presence of a hexamethylene ring in camphoric acid is considered as definitely proved. The reasoning given will apply also to a pentamethylene ring, though it must be admitted that a cis-trans, Δ^1 compound in a pentamethylene ring is not as probable as in a hexamethylene compound. The relationships which have been established thus far in my work will be clear from the accompanying table.

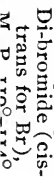
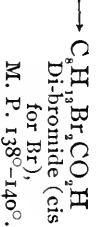
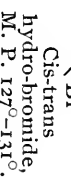
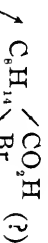
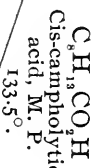
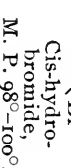
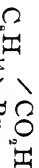
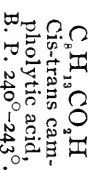
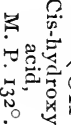
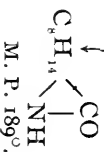
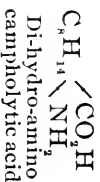
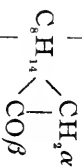
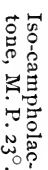
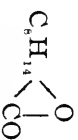
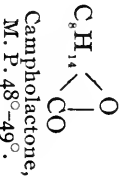
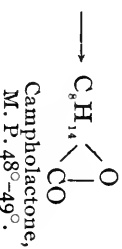
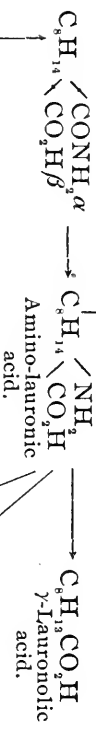
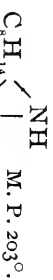
Di-hydro-hydroxycampholytic Acid.

The decomposition of di-hydro-amino-campholytic acid with nitrous acid is best effected as follows. 20 grams of the acid are dissolved in 19 cc. of dilute sulphuric acid (1:5) and 60 cc. of water, the solution is cooled and the calculated amount

¹ See Baeyer: Ann. Chem. (Liebig), **269**, 156.

² *Ibid.* **271**, 270.

³ Ber. d. chem. Ges., **27**, 2002.



of a 20-per cent. solution of sodium nitrite is introduced carefully at the bottom of the flask by means of a pipette. If the sodium nitrite is added carelessly there is a considerable loss of oxides of nitrogen but, if the solution is added as stated, the reaction takes place slowly and with very little escape of nitrous fumes. When the reaction is nearly complete more sulphuric acid is added and the whole is allowed to stand as long as the evolution of nitrogen continues. The campholytic acid and part of the hydroxy acid separate as an oil. The whole is extracted two or three times with small quantities of ligroin, which dissolves the campholytic acid easily but leaves most of the hydroxy acid undissolved. The latter is then extracted from the solution with ether. The residue left on distilling the ether is recrystallized from water, or, better, from acetic ether.¹ The acid crystallizes in compact small crystals which melt at 132°. It is moderately soluble in water and ether, very difficultly soluble in ligroin, easily soluble in alcohol. The aqueous solution is stable toward potassium permanganate. Beckman's mixture² of sulphuric acid and potassium pyrochromate is without effect on the acid in the cold, and even on warming darkens but very slowly with it, indicating that the hydroxyl group is tertiary. This agrees with the interpretation which has been given of the decomposition of amino-lauroic acid,³ which must have the carboxyl group in the same position as the hydroxyl group in this acid. The acid gives with fuming hydrobromic acid the same hydrobromide, melting at 98°–100°, which is obtained from the cis-trans-campholytic acid. This hydrobromide is believed to be a "cis" compound for reasons which have been given. When the hydroxy acid is warmed with dilute sulphuric acid (1:1), or more slowly on simply standing with it in the cold, it is converted quantitatively into cis-campholytic acid. In spite of the ease with which this change takes place the free hydroxy acid may be distilled in a small tube with only a very trifling decomposition, the distilled acid being insoluble in ligroin and almost perfectly stable toward permanganate. The analyses of the acid were as follows:

¹ See Einhorn and Meyenberg: *Ber. d. chem. Ges.*, **27**, 2472.

² *Ann. Chem. (Liebig)*, **250**, 325. ³ *This Journal*, **16**, 509.

0.1458 gram of the acid gave 0.1224 gram H_2O and 0.3329 gram CO_2 .

0.1450 gram of the acid gave 0.1212 gram H_2O and 0.3344 gram CO_2 .

	Calculated for $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CO}_2\text{H} \\ \text{OH} \end{smallmatrix}$	I.	Found.
C	62.79	62.27	62.90
H	9.30	9.33	9.29

Cis-trans-Campholytic Acid.

This acid was first prepared by Walker,¹ and was referred to in my last paper. The acid has now been further characterized by the preparation of the hydrobromide and by its conversion into cis-campholytic acid.

Hydrobromide of Cis-trans-campholytic Acid.

(Cis- β -brom-di-hydrocampholytic Acid.)

This acid is formed from either di-hydro-hydroxy-campholytic acid or cis-trans-campholytic acid by treatment with fuming hydrobromic acid and a little ligroin. The acid separates very soon in crystalline form and may be filtered on asbestos and washed with *cold* water. It must be dried at once *in vacuo* to prevent decomposition. It is stable in dry air, but decomposes slowly in moist air. It may be dissolved in cold ligroin and crystallized by evaporation under diminished pressure. It then separates in small aggregates of rectangular plates. The acid is decomposed at once by alkalis, chiefly with the formation of cis-trans-campholytic acid. There is formed, at the same time, a small amount of an indifferent body, probably a hydrocarbon. Fittig² has shown that this decomposition is characteristic of acids having bromine in the β -position. The acid melts, with decomposition, at 98° – 100° . The cis position for bromine and carboxyl follows from the relation of the acid to cis-trans-campholytic acid.

0.1141 gram of the acid prepared from cis-trans-campholytic acid gave 0.0912 gram AgBr .

0.0176 gram of the acid prepared from the hydroxy acid gave 0.0141 gram Ag Br .

	Calculated for $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CO}_2\text{H} \\ \text{Br} \end{smallmatrix}$	I.	Found.
Br	34.04	34.01	34.09

¹ J. Chem. Soc., **63**, 488, (1893).

² Ber. d. chem. Ges., **27**, 2662.

Cis-Campholytic Acid.
(*Walker's Camphothetic Acid.*)

The formation of this acid was first observed when campholytic acid had been left for some time in contact with hydrobromic acid, and an attempt was made to crystallize the product obtained from warm ligroin. Soon afterwards, on boiling cis-trans-campholytic acid with dilute sulphuric acid, as Fittig¹ directs for $\beta\gamma$ unsaturated acids, it was found that the same product is formed. At a high temperature the transformation is accompanied by a considerable amount of decomposition. The transformation may be made almost quantitative by leaving cis-trans-campholytic acid in contact with dilute sulphuric acid (1 : 1) at ordinary temperatures for some days. The acid is best crystallized from alcohol, in which it is quite easily soluble. It separates from that solvent in long thick needles. From ligroin it crystallizes in rectangular plates, as was observed by Walker.² The acid is very difficultly soluble in water, one part of the acid requiring 5880 parts of water for its solution at 20°. It is easily soluble in ether. The molecular weight was determined by the depression of the freezing point of acetic acid.³

0.2584 gram of the acid dissolved in 9.247 grams acetic acid caused a depression of 0.70°.

0.4446 gram of the acid caused a depression of 1.17°.

	Calculated.	I.	Found.	II.
Mol. W.	154	155.6		160.2

That the acid is a true unsaturated acid and not the isomeric lactone is proved by the fact that it dissolves readily and completely in a cold solution of sodium carbonate and the solution decolorizes potassium permanganate instantly, while the lactones of this series are stable towards that reagent. The acid melts at 133.5°. The first analyses were with an acid crystallized from dilute alcohol and were not satisfactory. The last three were with an acid crystallized from ligroin.

¹ Ber. d. chem. Ges., **27**, 2667.

² J. Chem. Soc., **63**, 504.

³ In a private communication Dr. Walker states that he has obtained with benzene the values 182 and 190 (theory 182) for the molecular weight of the ethyl ester. The values in his paper were obtained by a student, and are evidently erroneous.

0.1768 gram gave	0.1475 gram	H ₂ O and	0.4498 gram	CO ² .
0.1580 " "	0.1306 " "	" "	0.4012 " "	" "
0.1780 " "	0.1455 " "	" "	0.4526 " "	" "
0.1641 " "	0.1345 " "	" "	0.4201 " "	" "
0.0869 " "	0.0726 " "	" "	0.2223 " "	" "

	Calculated for C ₈ H ₁₃ CO ₂ H	I.	II.	Found. III.	IV.	V.
C	70.13	69.38	69.25	69.44	69.82	69.77
H	9.09	9.27	9.18	9.08	9.10	9.28

The last analysis was made with an acid obtained by the action of hydrobromic acid on the *cis-trans*-campholytic acid.

The *barium* salt of the acid is described by Walker¹ as containing five molecules of water. I have not been able to obtain a salt of that composition. The salt deposited from the hot solution during evaporation on the water-bath contains very little water, one and one-half per cent. being found. The salt deposited on cooling the hot solution contains water of crystallization but loses it so readily in a warm room that the number of molecules present could not be satisfactorily determined. In two cases the salt pressed between filter-paper lost 27.37 per cent. and 20.76 per cent. at 135°. Nine molecules of water would correspond to 26.78 per cent.

0.0780 gram of the salt dried at 135° gave 0.0405 gram BaSO₄.

	Calculated for (C ₈ H ₁₃ CO ₂) ₂ Ba.	Found.
Ba	30.92	30.94

After the work described in this paper had been completed, the possibility suggested itself that the *cis*-campholytic acid here described might be identical with the *iso*-lauronic acid of Koenigs and Hoerlin.² The oxidation of the acid with potassium permanganate gave *isolauronic* acid,³ melting at 134° (Koenigs and Meyer gives 132°) and the latter gave the yellow phenylhydrazide, melting at 199°, thus establishing the identity of the two acids beyond question, though some of the statements of Koenigs and Hoerlin do not agree very well with my observations. The *iso*-lauronic acid obtained was analyzed.

¹ *Loc. cit.*

² Ber. d. chem. Ges., **26**, 814.

³ *Ibid*, **27**, 3467.

0.1672 gram gave 0.1093 gram H_2O and 0.3918 gram CO_2 .

	Calculated for $\text{C}_9\text{H}_{12}\text{O}_3$.	Found.
C	64.28	63.91
H	7.14	7.26

As Koenigs and Hoerlin seem to be in doubt whether their acid may not be a lactone, and did not obtain correct values for an unsaturated acid in their analyses of salts, the calcium salt has been prepared and analyzed. The salt is decomposed by carbon dioxide, as stated in their paper, and in preparing it care is required to prevent its contamination with the free acid. The salt is deposited, on evaporating its solution in vacuo, in fine needles which lose their water easily over sulphuric acid. The salt, air-dried for a very short time, gave the following results:

0.0377 gram lost 0.0059 gram H_2O at 135° and gave 0.0121 gram CaSO_4 .

0.0832 gram lost 0.0131 gram H_2O at 135° and gave 0.0273 CaSO_4 .

	Calculated for $(\text{C}_8\text{H}_{13}\text{CO}_2)_2\text{Ca} + 3\frac{1}{2}\text{H}_2\text{O}$.	I.	Found. II.
$3\frac{1}{2}\text{H}_2\text{O}$	15.40	15.65	15.74
Ca	9.78	9.44	9.64

As I have shown the close relation which exists between campholytic acid and this acid, and as I have discovered another acid which bears a similar close relation to lauronolic acid, it seems desirable to name this acid iso-campholytic acid or cis-campholytic acid, and to give the name iso-lauronolic acid to the acid described in the latter part of this paper.

Di-bromide of Cis-campholytic Acid.

Two grams of the cis-campholytic acid were dissolved in a small amount of chloroform and the solution was cooled with a freezing mixture. A little more than the theoretical amount of bromine, dissolved in a little chloroform, was added slowly and the whole allowed to stand for a short time. The chloroform was then evaporated under diminished pressure, a little ligroin added, and the evaporation repeated till the bromide separated in crystalline form. As thus prepared, the acid consists of microscopic white crystals, which are very difficultly soluble in ligroin. There is formed, also, a considerable

quantity of an oil which is easily soluble in ligroin. The acid melts with decomposition at 138° – 140° . The dibromide is decomposed by a solution of sodium carbonate with the separation of an indifferent body which is insoluble in caustic soda. This decomposition is characteristic of $\alpha\beta$ dibrom acids.

0.1152 gram of the acid gave 0.1391 gram AgBr.

0.1022 gram of the acid gave 0.1224 gram AgBr.

	Calculated for $C_8H_{13}Br_2CO_2H$.	I.	Found. II.
Br	50.95	51.38	50.97

Hydrobromide of Cis-campholytic Acid.

(*Cis-trans- β -brom-di-hydro-campholytic Acid.*)

In one instance there was obtained by the action of fuming hydrobromic acid on cis-campholytic acid a hydrobromide which melted at 127° – 130° and which gave, on analysis, 34.85 per cent. of bromine. Repeated attempts to obtain the same acid a second time were unsuccessful, though the conditions were varied, and in one case glacial acetic acid saturated with hydrobromic acid was used. An acid melting at 110° – 115° was obtained several times and in one case was analyzed, giving 32.89 per cent. of bromine. Theory requires 34.04 per cent. Recrystallization from ligroin did not change the melting of either specimen. Solution in warm glacial formic acid caused the specimen melting at 110° – 115° to decompose. It is evident that the acid combines with hydrobromic acid with difficulty, but it is believed that the body melting at 127° – 130° consisted chiefly of the true hydromide of the acid.

Many attempts have been made with each of the campholytic acids to obtain from them benzene derivatives by heating in sealed tubes with the calculated amount of bromine in accordance with the method which has been used successfully by Einhorn and Willstätter.¹ Even at 100° the bromine is completely decolorized, but no simple reaction-product could be obtained. At temperatures approaching 200° there was a considerable amount of carbonization. I attach little weight to the negative result as bearing on the constitution of camphoric acid.

¹ Ann. Chem. (Liebig), 280, 88.

Hydrocarbon C₈H₁₄.

In my last paper it was stated that the decomposition of amino-laronic acid with nitrous acid yields an unsaturated acid, a lactone, a hydrocarbon, and carbon dioxide. The products have now been more carefully studied. Approximately 10 per cent. of the amino acid is decomposed in such a manner as to yield the hydrocarbon. The body is a clear, colorless liquid with a turpentine-like odor. It boils at 122°. Its specific gravity is 0.8033 at 15° and 0.8004 at 20°, referred, in each case, to water at the same temperature. It is probably the same hydrocarbon as that recently observed by Aschan,¹ but different from that of Koenigs and Meyer.²

0.1016 gram gave 0.1169 gram H₂O and 0.3240 gram CO₂.

	Calculated for C ₈ H ₁₄ .	Found.
H	12.63	12.68
C	87.27	86.97

When 4 atoms of bromine are added carefully to the hydrocarbon and the mixture is heated to 200° in a sealed tube the whole is carbonized. This resembles the conduct of some pentamethylene derivatives as observed by Perkin,³ but when we recall the conduct of turpentine toward bromine⁴ the result cannot be considered as important.

Iso-campholactone.

This body has not been obtained in sufficient amount for a satisfactory analysis. It has, however, been thoroughly characterized as a lactone by its insolubility in sodium and potassium carbonates, by conversion into the barium salt of the corresponding hydroxy acid, and by regeneration on boiling the latter with dilute hydrochloric acid. The body may be crystallized, at a low temperature, from a very little ligroin. It melts at 23° and is, therefore, isomeric and not identical with the campholactone of Fittig and Woringen.⁵ At it will be shown that γ -lauronic acid can be converted into the latter lactone, the two lactones are probably stereoisomers. Both lactones are stable toward potassium permanganate.

¹ Ber. d. chem. Ges., **27**, 3507.

² *Ibid.*, **27**, 3470.

³ J. Chem. Soc., **51**, 247, and **65**, 979.

⁴ See Kekule: Ber. d. chem. Ges., **6**, 438.

⁵ Ann. Chem. (Liebig), **227**, 10.

γ-Lauronolic Acid.

This acid was described in my last paper and the analysis of its calcium salt was given. A name was not given to the acid as it then seemed possible that the acid was identical with the lauronolic acid of Woringer.¹ The latter acid has recently been prepared by Aschan² and the fact that its calcium salt contains 3 molecules of water has been confirmed, and the acid been further characterized by the preparation of its amide. As in both respects the acid differs from that which I have obtained, the two acids must be considered as isomeric. The new acid would naturally be named iso-lauronolic acid but, unfortunately, this name has already been given to another acid by Koenigs³ and the name *γ*-lauronolic acid appears to be the best available, unless the name of Koenigs' acid is changed as suggested in this paper and as seems desirable.⁴

When the acid is warmed on the water-bath and shaken for a short time with dilute sulphuric acid, it is converted in part, into the campholactone of Woringer. This characterizes the acid as a *β γ* unsaturated acid.

The amide was prepared as follows: The dry acid, obtained from the crystallized calcium salt, was cooled with a freezing mixture, and a little more than the theoretical amount of phosphorus pentachloride was added. After the reaction was complete the products were poured carefully into cooled aqueous ammonia (0.90). The amide which separated would not solidify at -20° though it became very viscous. From the solution in water it separated, on spontaneous evaporation, in oily drops. It was shown by analysis that the amide had really been formed.

0.1016 gram of the amide gave 0.00897 gram N.

Calculated for $C_{18}H_{33}CONH_2$.		Found.
N	9.15	8.83

¹ *Ibid.*, **227**, 6.

² Ber. d. chem. Ges., **27**, 3504.

³ Ber. d. chem. Ges., **27**, 3346, and **26**, 814.

⁴ *γ*-Lauronolic acid has also been described and further characterized by Walker and Henderson under the name of allo-campholytic acid (J. Chem. Soc., 1895, 341).

Campholactone.

This is formed when γ -lauronic acid is warmed at 100° for a short time with dilute sulphuric acid. It was purified by shaking with a solution of potassium carbonate and conversion into the barium salt of the corresponding hydroxy acid. The latter was analyzed.

0.2209 gram of the salt dried at 105° gave 0.1056 gram BaSO_4 .

	$(\text{C}_8\text{H}_{14}\text{CO}_2\text{OH})_2\text{Ba}$	Found.
Ba	28.60	28.12

The lactone, regenerated from the salt, melted at 48° – 49° and is undoubtedly identical with the campholactone of Woringer.¹ As he states that lauronic acid is also formed when the lactone is regenerated from its salts the close connection between γ -lauronic acid and lauronic acid is established. The two acids are probably stereoisomers.

Several attempts have been made to secure the hydroxy acid corresponding to amino-lauronic acid but without success. Possibly, because its hydroxyl group would be that of a secondary alcohol, it is easily oxidized. In one case a small amount of an acid which melts at about 180° was obtained. A combustion made with a not very pure specimen of the acid gave 50.79 per cent. carbon and 6.88 per cent. hydrogen.

Possibly this is $\text{CH}_3-\overset{\overset{\text{CO}_2\text{H}}{|}}{\underset{\underset{\text{CO}_2\text{H}}{|}}{\text{C}}}-\text{CH}_2-\overset{\overset{\text{CH}_3}{|}}{\text{CH}}-\text{CH}_2-\text{CO}_2\text{H}$, which

would be formed by the oxidation of lauronic acid if it has the formula which I have spoken of as probable. Such an acid would require 49.54 per cent. carbon and 6.42 per cent. of hydrogen. A study of the oxidation products of γ -lauronic acid may throw further light on the matter.

TERRE HAUTE. February 26, 1895.

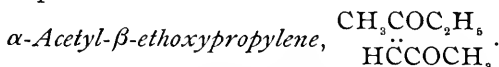
¹ *Loc. cit.*

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON SOME EXPERIMENTS WITH ACETYLACETONE AND ACETACETIC ETHER.

BY RICHARD S. CURTISS.

Nef has shown¹ that when silver acetylacetone is treated with ethyl iodide, an oil is obtained which is a mixture of two products; the one is neutral, the other soluble in sodium hydroxide, and the boiling-point of each is 175°–180°. I have carried out the experiment with larger quantities, and analyzed both products thus obtained.



The silver salt was prepared by adding concentrated aqueous argentic nitrate (one molecule) to an ice-cold aqueous solution of sodium acetylacetone (1:6). The silver salt has all the properties ascribed to it by Nef. 87 grams were obtained from 65 grams of sodium salt.

The silver salt (27.2 grams) was added to an excess of ethyl iodide (35 grams), care being taken to keep the temperature below 30°. After standing for 30–35 hours, the excess of ethyl iodide was distilled off, and the residue extracted with ether. The acid products of the reaction were extracted from the ethereal filtrate by means of dilute sodic hydrate (at 0°), and the alkaline solution, acidified and extracted with ether, gave 4 grams of an oil, which was found to be a mixture of acetylacetone and of α -ethylacetylacetone, (see below).

The ethereal solution, containing only the neutral products of the reaction, was found to contain an oil (4 grams), boiling between 68° and 70° at 15 mm. pressure. The oil thus obtained tenaciously holds small quantities of ethyl iodide, as shown by analysis, which can only be removed by repeated fractional distillation, or by digestion with a small amount of silver acetylacetone.

A product distilled twice and boiling at 71.5°–72° at 15 mm. pressure, gave the following results on analysis:

¹ Ann. Chem. (Liebig), 277, 73.

0.2084 gram substance gave 0.4961 gram CO_2 and 0.1790 gram H_2O .

	Theory for $\text{C}_7\text{H}_{12}\text{O}_2$.	Found.
C	65.62	64.92
H	9.37	9.54

The substance obtained is thus a mono-ethylated acetylacetone. It is a neutral oil with fragrant odor, turning light green on standing. From its properties there can be no doubt that the substance is α -acetyl- β -ethoxypropylene, formed from silver acetylacetone by the direct replacement of the silver atom. The substance reacts with great violence with bromine in dilute chloroform solution and hydrobromic acid is evolved, but no study was made of the products formed.

The acid products (4 grams), formed by the action of ethyl iodide on silver acetylacetone, are acetylacetone and α -ethylacetylacetone. These can be separated by shaking in ether solution with aqueous sodium carbonate (at 0°), in which the former substance—a much stronger acid than the latter—dissolves. The acetylacetone obtained boiled at 140° – 141° and was converted into the copper salt, (m. p. above 270°). The part insoluble in soda, after two distillations at reduced pressure, boiled at 64° – 67° at 12–15 mm. pressure, and gave the following figures on analysis:

0.2548 gram substance gave 0.6109 gram CO_2 and 0.2212 gram H_2O .

	Theory for $\text{C}_7\text{H}_{12}\text{O}_2$.	Found.
C	65.62	65.39
H	9.37	9.64

This substance α -ethylacetylacetone has already been obtained by Combes¹ from sodium acetylacetone and ethyl iodide (by heating in a sealed tube to 140°). In addition to the properties mentioned by Combes, which were confirmed, it forms, on shaking with aqueous copper-acetate solution, a well-defined copper salt. The salt is insoluble in water; nearly so in ligroin; very slightly soluble in cold alcohol, ether, carbon bisulphide, and benzene, but much more readily soluble on

¹Ann. chim. phy., [6] 12, 247.

warming. It is easily soluble in cold chloroform. For the analysis it was crystallized from hot alcohol, from which it separates out, on cooling, in long silky greyish-green needles, or in hair-like threads. It melts at 210° – 212° with previous browning at 205° .

Analysis: 0.3184 gram substance gave 0.0793 gram Cu_2S .

Theory for $\text{C}_{14}\text{H}_{22}\text{O}_4\text{Cu}$.		Found.
Cu	19.92	19.89

The only logical and consistent explanation possible of the action of ethyl iodide on silver acetylacetone, CH_3COAg
 $\text{HC}\cdot\text{COCH}_3$,
 is the following: The molecule has two points about equally susceptible of attack, namely, the silver atom, and the double bond between the two carbon atoms. In consequence thereof a direct replacement of the silver by ethyl takes place, as well as an addition of ethyl iodide to doubly bound carbon atoms,¹ resulting thus in the formation of α -acetyl- β -ethoxypropylene and α -ethylacetylacetone.

The Action of Hydrochloric Acid and Alcohol on Acetacetic Ether.

Notwithstanding the fact that Nef has clearly demonstrated the close analogy existing between the oxymethylene compounds and acetacetic ether in the free state, Claisen in a later paper² still maintains, without any apparent reason, his former position, that these compounds behave in a totally different manner. The points of difference brought forward by Claisen have been met *seriatim* and fully³ by the experiments of Nef and Bernhard⁴—with one exception: Claisen states that his oxymethylene compounds, like the fatty acids, are converted by means of hydrochloric acid and alcohol into their esters. I have therefore undertaken, at the suggestion of Dr. Nef, to show that the same is true of acetacetic ether:

66 grams acetacetic ether (1 molecule) were dissolved in 12 molecules of absolute alcohol and a steady current of dry hydrochloric acid gas passed, for ten minutes, into the solu-

¹ Nef: Ann. Chem. (Liebig), **276**, 200; **277**, 59.

² Ann. Chem. (Liebig), **281**, 311.

³ Ann. Chem. (Liebig), **276**, 238.

⁴ Ann. Chem. (Liebig), **282**, 173, 177.

tion cooled to -10° . After standing for forty-eight hours at ordinary temperature, the mixture is poured into much cold water, extracted with ether, the ethereal solution well washed with ice-cold sodic hydrate, and then dried with fused potassium carbonate. After distilling off the ether a yellow, fragrant oil is left, which, on cooling, solidifies. Large colorless, tabular crystals were obtained, melting at 30° , identical in every respect with Friedrich's β -ethoxycrotonic ether.¹

Analysis.—0.1843 gram substance gave 0.1479 gram H_2O , and 0.4097 gram CO_2 .

	Theory for $C_8H_{14}O_3$.	Found.
C	60.76	60.63
H	8.86	8.91

The yield obtained in the above experiment was 15 per cent. of the acetacetic ether taken. In another experiment where 6 molecules of alcohol were used to one of acetacetic ether, and anhydrous copper sulphate was present as a dehydrating agent, the same yield was obtained.

Freer has shown² that acetacetic ether absorbs hydrobromic acid forming an unstable hydrobromide. I have found that on passing dry hydrochloric acid gas into pure acetacetic ether (50 grams) cooled to -10° until the gas is no longer absorbed (one and a half hours) that the increase in weight (13.5 grams) corresponds to the formation of a hydrochloride. The theoretical increase would be 14.03 grams. On pouring this mixture into a cold alcoholic solution of sodium ethylate (1 molecule), and then working up as above, about 10 grams of a neutral oil were obtained, two-thirds of which consisted of β -ethoxycrotonic ether (melting-point 30°). A higher-boiling oil containing chlorine was also present.

On allowing 11 grams of acetacetic ether and 22 grams of absolute alcohol to stand at ordinary temperature for one week and then working up as above, 0.5 gram of β -ethoxycrotonic ether (melting-point 30°) were obtained. No better yield was obtained on heating the mixture in a sealed tube at 150° – 200° ; in this case carbon dioxide was evolved.

These experiments suffice to show clearly that acetacetic

¹ Ann. Chem. (Liebig), **219**, 333. Claisen: Ber. d. chem. Ges., **26**, 2731.

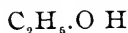
² J. prakt. Chem., [2] **47**, 239.

ether with alcohol, alone or in the presence of hydrochloric acid gas, is converted, like a fatty acid or the oxymethylene compounds, into its ester. The reason why the yield is not greater or even quantitative is due to the instability of the ester: it is split very readily by alcoholic hydrochloric acid into acetacetic ether and alcohol. An alcoholic solution of the substance treated with ferric chloride gives at first no color, but very soon (four to five seconds) a deep red coloration sets in, which is due to the formation of acetacetic ether.

Claisen states¹ that he has succeeded in obtaining β -ethoxycrotonic ester from acetacetic ether by means of what he calls "ein eigenthümliches Aethylirungsverfahren." It consists² in treating acetacetic ether with orthoformic ether and acetyl chloride. It is now perfectly clear that this is simply an esterification of acetacetic ether due to the presence of hydrochloric acid and alcohol in the reaction.

The Action of Bromine on β -Ethoxycrotonic Ester.

10 grams β -ethoxycrotonic ester, diluted with an equal volume of absolute ether or of carbon tetrachloride, and cooled to -10° , absorbs bromine (1 molecule) with a great evolution of heat. Hydrobromic acid is noticed after the addition of a few drops of bromine, showing that the di-bromide



$\text{CH}_3 \cdot \dot{\text{C}} \cdot \dot{\text{C}} \cdot \text{COOR}$ does not long exist at this temperature.



This is borne out completely by the further study of the complex reaction. The ethereal solution was allowed to evaporate over sulphuric acid and stick potash *in vacuo*, and the residual oil (16 grams) distilled at reduced pressure: 3 grams were obtained boiling from 110° to 115° at 18 mm.; 7 grams boiling from 125° to 127° at 16 mm.; and 2 grams boiling from 127° to 134° at 16 mm. These oils are all of a neutral or an acid nature, and therefore the acid constituents were removed by shaking in ether solutions with dilute sodium hydroxide at 0° , and the alkaline solution immediately acidified. The neutral portion on distillation *in vacuo*, boiled from 100° to 140° at 18 mm. and is undoubtedly a mixture

¹ Ann. Chem. (Liebig), **277**, 167. ² Ber. d. chem. Ges., **26**, 2731.

of α - and γ -brom- β -ethoxycrotonic esters, $\text{CH}_3\text{.C.}(\text{OC}_2\text{H}_5)\text{:CBr.COOR}$ and $\text{CH}_2\text{Br.C.}(\text{OC}_2\text{H}_5)\text{:CH.COOR}$.

The acid portion (6 grams) on distillation boiled from 100° to 118° at 16 mm., but the chief portion boiled from 112° to 115° . It behaves precisely like a mixture of α - and γ -brom-acetacetic ether. That γ -bromacetacetic ether was present in the mixture was proved by the isolation of the characteristic copper salt by means of copper acetate. It was not possible to isolate the copper salt of α -bromacetacetic ether in a pure state from the above mixture as it is a very unstable compound (see below).

The formation of the above complex mixture on treating β -ethoxycrotonic ester with one molecule of bromine is self-evident from the previous experiments of Nef.¹ The di-bromide of this compound, $\text{CH}_3\text{.CBr.OC}_2\text{H}_5$, does not exist at -10°

but splits spontaneously into α -brom- β -ethoxycrotonic ester, $\text{CH}_3\text{.C.OC}_2\text{H}_5$, which, as well as the β -ethoxycrotonic $\text{C}_2\text{H}_5\text{O}_2\text{C.C.Br}$

ester, $\text{CH}_3\text{.C.OC}_2\text{H}_5$ present at first in excess, is in part split by the hydrobromic acid given off into α -bromacetacetic ether, $\text{CH}_3\text{.C.OH}$, and acetacetic ether, $\text{CH}_3\text{.C.OH}$. On $\text{RO}_2\text{C.C.Br}$ $\text{H.C.CO}_2\text{R}$

the addition of more bromine this must act on the various substances present, and give rise to the formation of at least four products.

The Action of Bromine on Acetacetic Ether.

Nef has shown,² with great precision, that when acetacetic ether is treated with one molecule of bromine, either in ether solution (Duisberg) or in chloroform solution, a mixture of about equal quantities of α - and γ -bromacetacetic ethers is formed. Hantzsch,³ in view of the experiments of Epprecht,⁴ has attempted to throw some doubt on these experiments of Nef. At the present time the facts known are sufficient to ex-

¹ Ann. Chem. (Liebig). **276**, 236; **277**, 76.

² Ann. Chem. (Liebig). **266**, 77.

³ *Ibid.* **278**, 65-69. ⁴ *Ibid.* **278**, 69.

plain fully the different results obtained by various observers on this subject.

Hantzsch¹ has observed that pure α -bromacetacetic ether goes over on long standing into γ -bromacetacetic ether, and recently he has shown² that this change takes place very quickly in the presence of hydrobromic acid.

Nef in his experiments³ followed the directions of Duisberg: "Nur wurde *sogleich* mit Wasser versetzt und die aetherische Lösung mit Wasser gewaschen," etc. It is evident that he thereby removed the α -bromacetacetic ether from the action of the hydrobromic acid, and that other observers, by working less carefully and failing to remove the hydrobromic acid, might thus have converted the α -brom-compound at first present completely into the γ -brom-compound.

It is also noticeable in the original table of Nef⁴ that the crude bromacetacetic ether (*i. e.*, well washed and dried, but *not* distilled) gave more diacetosuccinic ether (4 grams from 14 grams oil) on treatment with sodium acetacetic ether than the distilled product of Duisberg (2.3 grams from 13.5 grams oil). This shows that, on distilling, a partial conversion into the γ -product takes place, and by continued distillation it is quite possible that the α -brom-compound is completely destroyed or converted into the γ -product.

In view of the fact that α - and γ -bromacetacetic ethers form copper salts which differ very greatly from one another as regards solubility in most organic solvents, I undertook some additional experiments with Duisberg's bromacetacetic ether in the hope of actually isolating the α - and γ -brom-products through their copper salts, and determining thus the relative amount of each constituent present.

The experiments seemed at first extremely promising. They failed however in the last-named object because of the great instability of the copper salt of α -bromacetacetic ether, and the fact that it is impossible to get a quantitative precipitation of either salt.

The copper salt of α -bromacetacetic ether (the latter prepared by Schönbrodt's method,⁵ and boiling from 101°–104° at

¹ Ber. d. chem. Ges., **27**, 355. ² *Ibid.*, 3168.

³ Ann. Chem. (Liebig), **266**, 80. ⁴ *Ibid.*, 87.

⁵ Ann. Chem. (Liebig), **253**, 175.

14 mm. pressure) was prepared by shaking the oil, in the presence of a small quantity of alcohol, with aqueous copper acetate. It comes out, if the proportion of alcohol has been well chosen, as a green, granular precipitate which, after being thoroughly washed with water and 50-per cent. alcohol, and dried *in vacuo*, has no sharp melting-point but decomposes between 125° and 135° , according to the rapidity of heating.¹

The salt is very unstable if not perfectly pure and dry. It is quite soluble in alcohol, ether, and carbon bisulphide; in chloroform and benzene it is very readily soluble; in ligroin (70° – 80°) it is difficultly soluble. The solutions in all except the last solvent are colored a deep grass-green. The alcoholic solution decomposes on standing or on being heated.

It was found that a preparation of Schönbrodts' pure α -brom-acetacetic ether, after being kept for ten days in a tightly corked tube, gave with copper-acetate solution a salt which consisted chiefly of copper γ -bromacetacetic ether,² showing how very readily this substance is converted into the isomer. The copper salt of γ -bromacetacetic ether can readily be obtained from Duisberg's bromacetacetic ether by shaking it in alcoholic solution with aqueous copper acetate. The following attempt, among many others, was made to prove that Duisberg's bromacetacetic ether is a mixture of the α - and γ -brom-substitution-products: 50 grams of the crude undistilled oil were dissolved in 40 cc. of chloroform and the mixture shaken thoroughly for some time with an excess of aqueous copper acetate; 30 grams of copper salt separated out which, washed with water and cold ether, decomposed and melted at 163° – 163.5° . 25 grams of this salt were converted, by means of shaking with dilute sulphuric acid and ether, into the free acid, and 20 grams of the oil obtained. This, on fractional distillation, boiled from 118° – 120° at 13 mm. pressure, and was the pure γ -bromacetacetic ether.³ The copper salt obtained from it has the following properties: It decomposes sharply at 161.5° – 162° ⁴; it is of a Paris-green color; it is insoluble in ligroin (70° – 80°); very difficultly soluble in abso-

¹ Hantzsch gives the point of decomposition at 140° .

² Cf. Hantzsch: Ber. d. chem. Ges., **27**; 355, 3168.

³ Cf. Epprecht: Ann. Chem. [Liebig], **278**; 77.

⁴ Hantzsch [Ber. d. chem. Ges., **27**; 355], gives the point of decomposition as 164° .

lute ether and alcohol; it is moderately soluble in benzene, more readily in chloroform. The solutions are very faintly tinted light green, except the chloroform solution, which is dark grass-green. An analysis gave:

	Found.	Theory.
Cu	13.30	13.19

The dark green chloroform filtrate from the above salt gave on evaporation *in vacuo* 15 grams of oil. This was dissolved in a small quantity of alcohol, and fractionally precipitated by gradual and alternate additions of aqueous copper acetate and alcohol, along with thorough shaking. The first precipitate obtained, after being well washed with water and 50-per cent. alcohol, decomposed between 120° and 138°. The second precipitate obtained decomposed from 128° to 130°. The salts thus obtained when freed from traces of γ -brom isomer by fractional crystallization from ether, resembled *perfectly in solubility and behavior* the copper salt obtained from pure α -brom-acetacetic ether.

There can therefore be no question from these experiments of the presence of a considerable amount of α -bromacetacetic ether in Duisberg's "bromacetacetic ether." A sharp determination of the relative amounts of the two constituents present in Duisberg's product could however not be attained, for reasons already given.

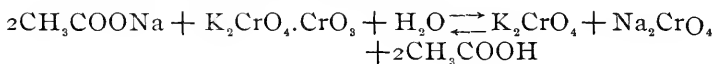
This, as above stated, has been determined approximately by the experiments of Nef, who in two ways showed that it is a mixture of about equal parts of α - and γ -bromacetacetic ethers.

ON THE DETERMINATION OF THE AFFINITIES OF ACIDS COLORIMETRICALLY BY MEANS OF POTASSIUM DICHROMATE.

BY J. H. KASTLE AND B. C. KEISER.

It was observed by one of us (Kastle) that the red color of a solution of potassium dichromate could be changed to the yellow color of the normal chromate by the addition of a moderately concentrated solution of sodium acetate. Such being the case, it was thought possible to utilize this reaction

for the determination of the affinities of acids colorimetrically, inasmuch as the reaction is that of the distribution of a base between 2 acids or, what is the same, between an acid and an acid salt; the reaction of the sodium acetate upon the dichromate being represented as follows:



In making the necessary observations it was found impossible to work with equimolecular solutions, for the reason that, not being able to obtain a normal solution of potassium dichromate, owing to its slight solubility, it was found necessary to use a tenth-normal solution of the acetate, and with this solution the changes in color were not sufficiently well marked to be determined by the means at our disposal without exceedingly large experimental errors. Hence it was found necessary, in most instances at least, to use normal solutions of the alkali salts of the several acids with tenth-normal potassium dichromate. The color comparisons were made in narrow glass cylinders, holding 30 cc., similar in shape to Nessler's cylinders, only of thinner glass and more nicely and accurately made. Experiments were made with the normal alkali salts of the following acids: Acetic, formic, butyric, benzoic, crotonic, monobromacetic, etc., the mode of procedure being as follows:

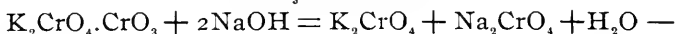
1 cc. of the tenth-normal dichromate is introduced into the measuring-cylinder with 10 cc., or some other suitable quantity, of a normal solution of the sodium or potassium salt of the acid whose affinity is to be determined. In order now to determine the extent of the change in color of the potassium dichromate and thereby the extent of decomposition of the salt, another cylinder, containing 1 cc. of the tenth-normal potassium dichromate is brought, by means of water and tenth-normal caustic soda, to the same dilution and color as the contents of the cylinder containing the tenth-normal dichromate and the salt of the acid. The tenth-normal caustic soda is of course added drop by drop, comparison being made between the two cylinders after the addition of each drop, until the two are as nearly alike in tint as possible. It should be said in this connection that, even by this rough

method of color-comparison, it is quite possible easily to detect differences in color caused by one drop of the tenth-normal solution of caustic soda even when the colors are almost of the same shade and tint. It is really astonishing to observe what minute differences in color can be distinguished between the yellow of the chromates and the red of the dichromates. The results obtained with the salts of the several acids employed are given below in Table I. 1 cc. of tenth-normal potassium dichromate was used in each experiment.

TABLE I.

No. of expt.	Sodium salt used.	Cc. of the N. sol. of salt used.	Cc. 0.1 N. NaOH required to produce same color with $K_2Cr_2O_7$ as salt.	Quantity of salt decomposed in grams.	Percentage decomposition.	Affinity.
1	Acetate	5	1.2	0.0090	2.19	44.0
2	"	10	1.5	0.0123	1.5	65.6
3	"	15	1.65	0.0135	1.09	90.7
4	"	20	1.7	0.0139	0.84	116.0
5	"	7	1.3	0.0106	1.85	53.0
6	Formate	10	0.65	0.0044	0.64	153
7	"	20	1.00	0.0068	0.5	199
8	"	30	1.1	0.0075	0.36	272
9	Butyrate	1	0.8	0.0064	6.4	11.5
10	"	2	1.2	0.0120	6.0	16.0
11	"	3	1.3	0.0130	4.33	22.1
12	"	5	1.6	0.0160	3.2	30.2
13	"	7	1.75	0.0175	2.5	39.0
14	Benzoate	10	0.8	0.0115	0.8	124
15	Brom-acetate	20	0.3	0.00483	0.15	665
16	"	10	0.25	0.00402	0.25	339
17	Crotonate	5	0.95	0.0102	1.8	51.6
18	"	10	1.3	0.0140	1.3	74.6
19	"	15	1.45	0.0152	0.93	102.0
20	"	20	1.55	0.0162	0.75	128.0

The percentage-decomposition of the salt of the acid whose affinity is to be determined, is calculated as follows: In experiment 1, for example, the alteration in color produced by 5 cc. normal sodium acetate was also brought about by 1.2 cc. tenth-normal caustic soda; hence in view of the action taking place



we have :

$$2\text{NaOH} : 2\text{CH}_3\text{COONa} = 0.0048 : x.$$

$x = 0.0090$ = the quantity of sodium acetate decomposed. Comparing this with the quantity of acetate started with we obtain the percentage-decomposition ; and, knowing the percentage-decomposition and, for the purposes of comparison, making the affinity of potassium dichromate equal to 1, the affinity of acetic acid, under the conditions of the above experiment, is equal to $1 \times \frac{100 - 2.19}{2.19} = 44$. This signifies that, at the dilution of the experiment and acting according to the relative masses of the two substances, the acetic acid is forty-four times as strong as potassium dichromate. In the same way the other members in the last two columns are obtained. If now we compare the numbers obtained for the several acids at corresponding dilutions, it is seen that these members bear to each other the same relation as do the numbers obtained by other observers for the affinities of these acids. The following arrangement brings out this relation very clearly :

Acid.	With 5 cc. N. sol.	7 cc.	10 cc.	15 cc.	20 cc.
Acetic	44	53	65.6	90.7	116
Formic	153.	199
Butyric.....	30.2	39
Benzoic.....	124
Crotonic.....	51.6	74.6	102.0	128
Monobromacetic	399.	665

An examination of these results reveals, further, that essentially the same relation exists between the numbers obtained for one quantity of the several salts used, and those obtained for other quantities. For example, the number found for crotonic acid, using 10 cc. of the normal solution of its sodium salt, is 74.6 ; for 5 cc. of the acetate and crotonate used, however, the numbers for acetic and crotonic acids are, respectively, 44 and 51.6. Hence by proportion, calculating upon the basis of the number found for acetic acid, where 10 cc. of sodium acetate are used—which is 65.6—we should obtain 76

as representing the strength of crotonic acid as compared with that of acetic, 65.6; thus

$$44 : 51.6 :: 65.6 : x; x = 76—$$

whereas the last term as determined experimentally is, as stated above, 74.6.

This signifies that the relative strength of these two acids is the same for a large as well as a small quantity of their salts used. In the same way the several values of crotonic acid as compared with acetic are as follows:

	x Calculated for crotonic acid.	x Found.
44 : 51.6 = 65.6 : x ;	76	74.6
44 : 51.6 = 90.7 : x ;	106	102.0
65.6 : 74.6 = 116 : x ;	131	128.0

In the same manner the following values are obtained for butyric, bromacetic, and formic acids:

	x Calculated for butyric acid.	x Found.
44 : 30.2 = 53 : x ;	36.4	39.0
	x Calculated for bromacetic acid.	x Found.
65.6 : 399 = 116 : x ;	705	665
	x Calculated for formic acid.	x Found.
65.6 : 153 = 116 : x ;	270	199

Except in the case of formic acid the differences in the results calculated and observed, come within the limit of the experimental error of the method employed for the color-measurement, and further, a comparison of the results obtained by this method with those of other methods for the determination of the affinities of acids, shows conclusively that this method affords a means of determining the relative strengths of certain of the monobasic acids. For the purpose of making such a comparison some of the numbers for the acids here employed are given along with those obtained by this method:

	I.	II.	III.	IV.
Acetic.....	1.23	0.43	0.35	65.6
Formic	3.9	1.68	1.31	153.0
Butyric.....	0.98	0.32	0.30	47.0
Benzoic ¹	124.0
Crotonic ²	74.6
Monochloracetic, and	7	4.90	4.3
hence, monobromacetic	7 [about]	4.90 [about]	4.3 [about]	3.99

¹ Formic acid is stronger than benzoic. For crotonic and benzoic acids see the numbers given in the article "Affinity"—Watts' Dictionary [New Edition].

² At certain dilutions acetic acid seems stronger than crotonic, whereas at others the reverse is true. These two acids have very nearly the same strength.

The numbers in column I in the above table were obtained by Ostwald by determining the distribution of a base between two acids; in II, by the method of electrical conductivities; in III, by the saponification of methyl acetate; in IV, by the colorimetric method herein described.

It will be observed that by means of the colorimetric method it is certainly possible to arrange these acids in the order of their strength; and in most cases the agreement between this and other methods is as close as could be expected of methods so entirely different. It is not claimed for the new method that it is as extensive or far-reaching or accurate as any of the methods now in general use. In the case of very strong acids, for example, whose salts it is impossible for the potassium dichromate to decompose, no exact results can be obtained. For example, 20 cc. of a 3 N. solution of potassium chloride was added to 1 cc. tenth-normal potassium dichromate without causing any appreciable change of color. Hence all that could be learned in cases of this kind would be that the acid was very strong as compared with acetic. With colored acids also it is obvious that no results could be obtained by this method. With dibasic acids also the results might be uncertain owing to the formation of acid salts; in fact certain results already obtained with a few of the commoner dibasic acids indicate that the numbers obtained for these acids are too low. The few monobasic hydroxy acids tried, lactic, salicylic, etc., gave unsatisfactory results, or perhaps it would be more in keeping with the facts to say that they gave no results at all, in that the color of the potassium dichromate remained unchanged after the addition of considerable quantities of a lactate or a salicylate. It is quite possible however, that the hydroxy portion of these acids is as strong or stronger than the potassium dichromate in which case there would be no change of color. It would thus appear that the relative strengths of a great many acids cannot be determined by the new method; nevertheless in consequence of its beauty and simplicity it is certainly not without interest. Even though applicable in comparatively few cases, it can doubtless be applied to all weak or moderately strong acids whose number is by no means inconsiderable. It possesses the further advantage that it can

be applied to the determination of the affinities of rather insoluble acids such as benzoic acid, etc., in concentrated solution, for the reason that oftentimes the more insoluble the acid the more soluble its alkaline salts. It is our purpose to test this method upon all classes of acids as soon as possible—making use of a colorimeter to insure the accuracy of the color-comparisons. Inasmuch, however, as the work cannot be done immediately, it is deemed advisable to submit the results already obtained as preliminary to a more extended investigation, believing that they are not altogether wanting in importance or interest.

STATE COLLEGE OF KENTUCKY, April, 1895.

Contribution from the Sheffield Laboratory of Yale University.

ON SOME AZO AND AZIMIDO COMPOUNDS.

BY W. G. MIXTER.

Benzoyl Metazoparatoluide.—Pure benzoyl *m*-nitro-*p*-toluide,¹ dissolved in alcohol, was subjected to the reducing action of zinc and ammonia until there was no further separation of the azo compound from the solution. The precipitate was washed with alcohol, digested with dilute hydrochloric acid to remove zinc, then washed with water, dried, and finally crystallized from glacial acetic acid. The yield was 50 per cent. of the nitrotoluide taken. The following is the analysis:

	C.	H.	N.
Calculated for $C_{28}H_{24}N_4O_2$	75.0	5.35	12.50
Found	75.17	5.50	12.71

Benzoyl metazoparatoluide, $[C_6H_5.(1)CH_3.(4)NHC_7H_5O.(5)N]_2$, is almost insoluble in alcohol, is sparingly soluble in boiling glacial acetic acid, from which it separates in orange-colored fibres as the solution cools. It melts at 242° . It yielded only an impure, tarry product when treated with alkalis or sulphuric acid to remove the benzoyl group.

Acetyl Metazoorthotoluide.—The acetyl *m*-nitro-*o*-toluide

¹ The nitro compound was prepared by adding crystallized benzoyl *p*-toluide to 10 parts of nitric acid having a density of 1.4. The mixture without warming was shaken for a time and then poured into water. The product, after crystallizing from alcohol, melted at 145° .

used was made by Mr. G. F. Campbell, who did not have time to finish the investigation commenced with it. He nitrated *o*-acetotoluide at the ordinary temperature with nitric acid of density 1.4. The product, crystallized from alcohol, melted at 202°. Beilstein and Kuhlberg² give the melting-point of 197° for the compound. The reduction was made in alcohol with zinc and ammonia. The azo compound separated slowly. It was washed with alcohol, hydrochloric acid, and water, and then dissolved in boiling glacial acetic acid. The solution, on cooling, yielded orange-colored fibres of the azo compound.

	C.	H.	N.
Calculated for $C_{18}H_{20}N_4O_2$	66.67	6.17	17.28
Found	66.62	6.17	17.24

Acetyl metazoorthotoluide, $[C_6H_3.(1)CH_3.(2)NHC_2H_5O.(5)N]_2$, does not melt at 310°, is almost insoluble in alcohol, and not very soluble in hot glacial acetic acid. Attempts to obtain pure *m*-azo-*o*-toluidine were not successful. The azotoluide was not decomposed by hydrochloric acid. It was therefore dissolved in warm sulphuric acid, the solution poured into water, and ammonia added. The precipitate which formed was washed with water and crystallized from alcohol in which it was very soluble. The product was dark red, melted at 199°, and yielded 21.88 per cent. of nitrogen, azotoluidine having 23.33 per cent. It formed deep red solutions with sulphuric and hydrochloric acids. Hydrogen platinum chloride gave in an aqueous solution of the chloride a bulky precipitate which, after washing and drying, was found to contain 2 per cent. less platinum than was calculated for the platinum salt of azotoluidine.

Benzoyl Azoxylide.—The benzoyl nitroxylide used in the investigation was made as follows: Benzoyl xylide from commercial xylidine and benzoyl chloride was added to nitric acid of density 1.4 and, when the temperature rose to 25° or 30°, the mixture was poured into water. By repeated crystallization from alcohol benzoyl nitroxylide melting at 187° was separated from products with lower melting-points. It yielded when saponified with sulphuric acid nitroxylidine,

$C_6H_2.(1)CH_3.(3)CH_3.(4)NH_2.(5)NO_2$, melting at 73° . The benzoyl nitroxylide was reduced in an alcoholic solution by zinc and ammonia, and the precipitate which separated was purified by washing and then dissolved in hot glacial acetic acid. The compound separated in orange-colored fibres as the solution cooled.

	C.	H.	N.
Calculated for $C_{30}H_{28}N_4O_2$	75.63	5.88	11.77
Found.....	75.42	5.83	11.85

Benzoyl azoxylide, $[C_6H_2.(1)CH_3.(3)CH_3.(4)NHC_7H_5O.(5)N_2]$, is slightly soluble in hot alcohol, and decomposes without melting at 280° – 290° .

In the preparation described of the azo derivatives of toluidine and xylylidine there separated from the alcoholic solution in which the reduction was made, no azoxy compound—which is the first product that may be formed when a nitro compound is reduced. This was doubtless due to the solubility of the azoxy compounds, since if they were formed and did not separate they would have been reduced to azo compounds. This view of the solubility of the azoxy compounds in question is supported by the observations of Bankiewicz¹ who found the acetyl-*m*-azoxy-*p*-toluide (acetamidoazoxytoluene) to be soluble in alcohol and the corresponding azo compound to be insoluble. The former he made by reducing acetyl nitrotoluide with ammonium sulphide and the latter with sodium amalgam in an acetic-acid solution. Mr. G. F. Campbell, of this laboratory, obtained acetyl-*m*-azo-*p*-toluide by reduction with zinc and ammonia, which was insoluble in alcohol and otherwise resembled Bankiewicz's compound. The acetyl and benzoyl derivatives of ortho-, meta-, and para-azoxyaniline,² I found to be insoluble, or nearly so, in alcohol. They separate when the nitro compounds from which they are made are reduced in alcoholic solution. The same is true of benzoyl *o*-azoxy-*p*-toluide,² but this is the only known insoluble homologue of benzoyl azoxyanilide or acetyl azoxyanilide. Acetyl azoanilide is soluble in alcohol, while

¹ Ber. d. chem. Ges., **22**, 1396.

² This Journal, **5**, 1, 282.

the homologues of it thus far obtained are insoluble. It is impossible as yet to make a rule regarding the solubility of the compounds in question, but this much appears to be indicated: If in benzoyl azoxyanilide or acetyl azoxyanilide one or more atoms of hydrogen of the benzene group is replaced by a radicle, the resulting compound is likely to be soluble in alcohol, while an insoluble compound results by a similar replacement in benzoyl azoanilide or acetyl azoanilide.

Benzoylazimidotoluene.—Azimidotolual was first obtained by Ladenburg,¹ who called it amidoazotoluylen. Boessneck² described the acetyl derivative, which was later obtained in two modifications by Zincke and Lawson,³ who prepared a number of derivatives of azimidotoluene. The benzoyl derivative is easy to prepare because of its stability and insolubility in water and dilute acids. In one experiment 7 grams of benzoyltoluidenediamine, made from benzoyl *m*-nitro-*p*-toluide, were dissolved in hot water containing 15 cc. of hydrochloric acid, and the solution was diluted to 2 liters to keep the diamine in solution when cool. Nitrous fumes were then passed into the solution, causing at once a turbidity. When the separation of the benzoylazimidotoluene was completed it was filtered off, washed and dried. The product weighed 6.4 grams. A more convenient way, which was used several times, is to add potassium nitrite to an acid solution of the diamine. Benzoylazimidotoluene dissolves easily in alcohol, from which it separates on evaporation of the solution in white fibres, melting at 125°. The following is the analysis:

	C	H	N
Calculated for $C_{14}H_{11}N_3O \dots$	70.89	4.64	17.72
Found	70.40	4.97	17.76

Benzoylazimidotoluene, $C_6H_5 \cdot (1)CH_3 \cdot (4)N:N \cdot (5)N \cdot C_7H_5O$ decomposes slightly after a time, as is apparent from the odor of benzoic acid, and is readily saponified by acids and alkalies, including ammonia. When heated with aniline, benzoyl anilide is formed; with phenylhydrazine, benzoylhydrazine results.

¹ Ber. d. chem. Ges., 9, 220.

² *Ibid.* 19, 1758.

³ Ann. Chem. (Liebig), 240, 110.

Azimidoxylyene.—Benzoyldiamidoxylyene, $C_6H_2.(1)CH_3.(3)CH_3.(4)NHC_6H_5O.(5)NH$, was dissolved in warm dilute hydrochloric acid, and after the solution had cooled potassium nitrite was added. A portion of the azimido compound formed separated and a part remained in the solution from which it was precipitated by neutralizing the acid present with ammonia. The product, after crystallizing from alcohol, melted at 111° and gave 16.79 per cent. of nitrogen, theory requiring 16.73 in benzoylazimidoxylyene, $C_6H_2.(1)CH_3.(3)CH_3.(4.5)N_3.C_6H_5O$.

One gram of another preparation of benzoylazimidoxylyene was treated with hot concentrated hydrochloric acid and water was added. The solution, on cooling, deposited benzoic acid, which was filtered off and to the filtrate ammonia was added in slight excess. Azimidoxylyene separated as a white powder, which was easily washed. After drying over sulphuric acid it melted at 196° . It was, however, not quite pure, as it yielded only 27.46 per cent. of nitrogen, against 28.56 required by the formula $C_6H_2.CH_3.CH_3.N_3H$. Another preparation, which melted at 186° , gave 28.28 per cent. of nitrogen.

Azimidoxylyene is slightly soluble in cold water, more soluble in hot water, from which it is deposited on cooling as a white meal. It is soluble in alcohol, in ether, in nitric acid, and in hydrochloric acid. The hydrochloric-acid solution does not give a precipitate with hydrogen platinic chloride. Azimidoxylyene is soluble in an excess of ammonia and separates when the ammonia is boiled off. Its acid character is also shown by its forming a silver salt. To a solution of it in nitric acid silver nitrate was added; a white curd precipitated which, after washing and drying, yielded 36.79 per cent. of silver; calculated for $C_6H_2.CH_3.CH_3.N_3.Ag$, 42.93 per cent. In another attempt to obtain the silver salt pure, an alcoholic solution of silver nitrate was added to an alcoholic solution of azimidoxylyene. A very bulky gelatinous precipitate formed, which was washed with water and dried at 100° . It was permanent in light. Silver was found in it to the extent of 44.8 per cent. The excess over the theoretical amount of silver is doubtless due to the difficulty in washing the salt.

Contributions from the Chemical Laboratory of the Lehigh University.

II—ON THE ACTION OF CERTAIN ALCOHOLS WITH METADIAZOBENZENESULPHONIC ACID.¹

BY W. B. SHOBER AND H. E. KIEFER.

One of us several years ago investigated the action of methyl, ethyl, and propyl alcohols upon paradiazobenzene-sulphonic acid.² As a result of that investigation it was found that, when the decomposition of the diazo compound was effected with methyl alcohol at diminished pressure, the course of the action was such as to give rise to the formation of the hydrogen compound only, benzenesulphonic acid; at ordinary and slightly increased pressures both benzenesulphonic acid and methoxybenzenesulphonic acid were formed, thus showing that the hydrogen- and alkoxy-reactions had both taken place.

When the diazo compound and the alcohol were heated in a sealed tube only the methoxy product was formed. When ethyl and propyl alcohols were used, the hydrogen product alone was formed. In view of these results and others which are recorded, it was desirable to determine the action of these same alcohols upon *meta*-diazobenzenesulphonic acid. The starting-point in this work was the preparation of *meta*-nitrobenzenesulphonic acid. Of the several methods given the one of Laurent³ was selected.

Pure benzene was converted into benzenesulphonic acid and this was treated with fuming nitric acid, giving rise to the formation of the three isomeric nitrobenzenesulphonic acids. After standing, the mass was poured into a large quantity of water. During this preparation it was found necessary to use nitric acid not stronger than that having a specific gravity of 1.5, and to keep the temperature low by continually plunging the flask into running water. In one

¹ From the thesis of H. E. Kiefer, submitted to the Faculty of the Lehigh University for the degree of Master of Science, June, 1894.

² This Journal, **15**, 379.

³ Jsb. Chem., 1850, 418.

case in which we used acid of specific gravity 1.6 and allowed the temperature to rise, almost the entire amount of benzene originally used was converted into metadinitrobenzene. The water solution was then neutralized with barium carbonate, filtered, and concentrated.

An attempt was made to separate the three barium salts by crystallization, as advised by Limpricht. The result was not satisfactory. The experiment was repeated. After removing the nitrobenzenes the acids were neutralized with pure barium carbonate. Repeated attempts to obtain good crystals failed. The barium salts were then converted into the potassium salts, these into the chlorides, and finally into the amides. The amides were separated by fractional crystallization. Each lot of crystals was repeatedly crystallized until a sharp melting-point was obtained. The metanitrobenzenesulphonamide melts at 161° , the para compound at 131° , and the ortho compound at 186° . There was no difficulty in making the separation in this manner. The meta amide was divided into 12-15 gram portions. Each portion with about an equal weight of concentrated hydrochloric acid was heated in a sealed tube for ten hours at a temperature of 150° .¹ The contents of the tube were then evaporated to dryness and the ammonium salt of metanitrobenzenesulphonic acid thus obtained, was recrystallized until it appeared in long colorless prisms. The crystals were dissolved in water strongly ammoniacal, and sulphuretted hydrogen passed into the solution until there was no further rise in the temperature of the mass. After removing the excess of ammonium sulphide and sulphur, the solution was acidified with hydrochloric acid and allowed to stand twelve hours, when the amido acid separated out in flat, white, flaky crystals. It crystallizes also in fine needle-like forms.

This metamidobenzenesulphonic acid was converted into the diazo compound by mixing the acid with a very small quantity of water and passing a rapid current of cooled nitrous fumes through the mass. When the mixture became

¹ In one experiment four tubes were placed in the furnace at the same time. At the end of eight hours one of them was partially filled with a very black liquid, which upon investigation was found to have the properties of a dye. Repeated attempts to obtain this substance again have failed.

clear, due to the solution of the diazo compound in the water, cooled alcohol was added, and it was allowed to stand in a freezing-mixture until the fine, yellowish needles of the diazo compound separated out. We found the compound to be very explosive, thus confirming Berndsen's observations,¹ although Meyer and Stüber² state that the compound is not explosive. As Berndsen has pointed out they were probably working with a mixture of the diazo compound and the amido acid which had escaped the diazotisation.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid under Diminished Pressure.—About 7 grams of the diazo compound and 100 cc. of dehydrated methyl alcohol were placed in a flask.³ The contents of the flask were heated to boiling on a water-bath for two and a quarter hours. At this point the suction was shut off, and the experiment could not be completed. When it was resumed after an interval of thirty-six hours, the decomposition was complete in a few minutes. During the experiment the pressure varied from 360 to 410 mm. of mercury (absolute pressure). The alcohol changed color until it was a deep amber tint. The solution was filtered, the alcohol distilled off, and the residue, after dilution with water, was neutralized with barium carbonate. The barium salt was converted into the potassium salt and this into the amide. Upon crystallizing, two amides were found, one of them separating out in long slender needles, the melting-point of which was found to be 128°. This substance is shown by the analysis given below to be methoxybenzenesulphonamide—presumably the meta modification, which we believe has not been described before. The other amide had a melting-point of 152°. From this fact and the conditions under which it was formed, it was concluded that the compound was benzenesulphonamide. These two amides were separated by mechanical means, and it was found that the methoxy amide had been formed in larger quantity than the hydrogen amide.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid at Ordinary Pressure.—7.5 grams of the diazo compound and

¹ Ann. Chem. (Liebig), 177, 88.

² Ibid. 165, 165.

³ For description of the apparatus see this Journal, 15, 324.

150 cc. of methyl alcohol were placed in a flask to which was attached a reflux condenser. The mixture was boiled on a water-bath; at the expiration of thirty minutes the decomposition was complete, the solution being a bright amber color. The decomposition-products were treated as before. Two amides were obtained, the methoxy compound being present in much larger quantity than the hydrogen compound.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid at 400 mm. Pressure.—5 grams of the diazo compound and 100 cc. methyl alcohol were placed in a pressure-flask¹ and heated. The reaction took place rapidly, the decomposition being complete in *seven* minutes. The resulting residue was converted into the amide as above. Upon crystallizing, two kinds of crystals were found, the melting-point of one being 128°, that of the other 152°—thus indicating that both reactions had taken place.

Action of Methyl Alcohol on Metadiazobenzenesulphonic Acid at 800 mm. Pressure.—6 grams of the diazo compound and 120 cc. methyl alcohol were heated on a water-bath at a pressure of 800 mm. mercury. The reaction was complete in ten minutes, the solution being a faint amber color. The products of decomposition were treated as before. Two amides were again found, the methoxy amide being present in great excess.

The methoxy compound was analyzed with the following results:

0.2024 gram substance gave 0.2156 gram BaSO₄ (Carius' method).

0.200 gram substance gave 0.3281 gram CO₂ and 0.0085 gram H₂O.

	Mol. wt.	Calculated for C ₇ H ₉ SN ₃ O ₃ .	Found.
C ₇	83.79	44.89	44.74
H ₉	9.00	4.82	4.92
S	31.98	17.13	17.08
N	14.01	7.51
O ₃	47.88	25.61
	<hr/> 186.66	<hr/> 100.00	

¹ For description of apparatus, see this Journal, 15, 106.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at Ordinary Pressure.—Berndsen¹ states that when metadiazobenzenesulphonic acid is boiled with absolute alcohol at the ordinary pressure, no action takes place. We cannot confirm this statement. Our first experiment was conducted as follows: 8 grams of the diazo compound prepared as described above, and 160 cc. of absolute alcohol² were placed in a flask to which was attached a reflux condenser. The flask was heated slowly; the reaction began almost immediately, and in seven minutes the decomposition was complete, leaving a clear solution of deep amber color. The experiment was repeated later with precisely the same results. The products of the decomposition were examined, as in the other cases, by converting the residue into the amides. Two kinds of crystals were found: one melting at 126°, which is shown by the analysis below to be ethoxybenzenesulphonamide; the other, melting at 149°, is benzenesulphonamide. The ethoxybenzenesulphonamide, presumably the *meta* modification, not having been described before was analyzed with the following results:

0.1878 gram substance gave 0.2194 gram BaSO₄ (Carius' method).

0.5 gram substance gave 0.3595 gram N (Kjeldahl-Gunning method).

	Mol. wt.	Calculated for C ₈ H ₁₁ SN ₃ O ₃ .	Found.
C ₈	95.76	47.72
H ₁₁	11.00	5.48
S	31.98	15.94	16.04
N	14.01	6.98	7.19
O ₃	47.88	23.88
	<hr/> 200.63	<hr/> 100.00	

Berndsen's inability to effect the decomposition of the diazo compound with absolute alcohol at ordinary pressure was probably due to the fact that the compound with which he worked was metamidobenzenesulphonic acid which had escaped diazotisation, and not metadiazobenzenesulphonic acid.

¹ Ann. Chem. (Liebig), **177**, 89.

² The alcohol had been allowed to stand over lime and afterwards over anhydrous copper sulphate for about two weeks.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at 400 mm. Pressure.—11 grams of the diazo compound and 200 cc. absolute ethyl alcohol were placed in a flask and treated as before. The reaction was energetic, the decomposition being complete in less than five minutes. Examination of the product revealed the presence of two different amides, one melting at 126° and the other at 150°.

Berndsen¹ decomposed the same diazo compound with absolute alcohol at the same pressure, but was unable to separate the two substances, and consequently unable to obtain the benzenesulphonamide in a pure condition. He says: "Dieses Sulfobenzolamid krystallisirte aus heissem Wasser in kleinen Nadeln oder Blättchen, aus Alkohol und Aether in kleinen sechsseitigen Prismen, *die aber noch durch eine klebrige Substanz verunreinigt waren* . . . Aber die Schwankungen im Schmelzpunkte zeigten, das kein reines Sulfobenzolamid vorlag, das bei 149° schmelzen soll, während verschiedene Krystallisationen meiner Verbindung bei Temperaturen schmolzen, die zwischen 139° und 159° lagen." The substance with which Berndsen worked was undoubtedly a mixture of ethoxybenzenesulphonamide and benzenesulphonamide.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at 800 mm. Pressure.—8 grams of the diazo compound and 160 cc. absolute alcohol were placed in the pressure-flask and heated rapidly until the manometer indicated a pressure of 800–820 mm. mercury. The action began almost immediately upon applying heat and was complete in less than five minutes. Upon converting the decomposition-products into the amides, it was found that both the ethoxy- and hydrogen-reactions had taken place. The hydrogen compound was present in very small quantity.

Action of Ethyl Alcohol on Metadiazobenzenesulphonic Acid at Diminished Pressure.—7 grams of the diazo compound and 145 cc. of absolute alcohol were placed in a flask on a water-bath and heated, the pressure being 440 mm. (absolute pressure). The reaction was complete in less than twenty minutes. The decomposition-products were treated as before. *Two* amides were found.

¹ Ann. Chem. (Liebig), 177, 91.

Action of Propyl Alcohol on Metadiazobenzenesulphonic Acid at an Increased Pressure.—6 grams of the diazo compound and 125 cc. of propyl alcohol which had been dehydrated over lime, filtered, and distilled, were placed in the pressure-flask and heated as rapidly as possible. Decomposition began at once. The pressure increased rapidly; when the manometer indicated 800 mm., the decomposition was complete. Length of time, seven minutes.

The decomposition in this case was more complicated than with the lower alcohols. The resulting liquid had a dirty-brown appearance, and the yield of the principal products was very much smaller. The residue was treated as in the other cases. Owing to the small quantity of amide obtained it was impossible to decide whether or not both reactions had taken place. A sufficient quantity of an amide was obtained however, to show that it had a melting-point of 122° , and to make a sulphur determination:

0.158 gram of the substance gave 0.170 gram BaSO_4 (Carius' method), corresponding to 14.78 per cent. of sulphur. The theory for propoxybenzenesulphonamide requires 14.90 per cent. of sulphur.

Action of Propyl Alcohol on Metadiazobenzenesulphonic Acid at Ordinary Pressure.—5 grams of the diazo compound and 100 cc. propyl alcohol were placed in a flask to which was attached a reflux condenser, and heated. The decomposition was complete in fifteen minutes. The products were treated as before. Upon crystallizing the amides, two were found, one melting at 122° and the other at 150° ; the latter was present in very small quantity.

SUMMARY.

I. Methyl alcohol at various pressures gives *both* reactions. At the highest pressures the methoxy compound is formed in greatest excess.

II. Ethyl alcohol gives similar results.

III. Propyl alcohol at ordinary pressures gives *both* reactions.

Comparing these results with those obtained by the decom-

position of *paradiazobenzenesulphonic acid*,¹ with the same alcohols under essentially the same conditions, we find that the *para* compound when decomposed with :

I. Methyl alcohol at reduced pressure gives *only* the hydrogen reaction.

II. At other pressures the *para* and *meta* compounds give similar results.

III. Ethyl alcohol gives *only* the hydrogen reaction.

IV. Propyl alcohol gives *only* the hydrogen reaction.

The metadiazo compound is decomposed with much greater ease than the *para* compound, the latter requiring with various alcohols at various pressures from two to eight hours, while with the former but a few minutes were usually required.

REPORT.

THE MOLECULAR COMPLEXITY OF LIQUIDS.

The study of the physical properties of substances in the form of vapor has resulted in the perfection of several methods for the determination of their molecular weights in that condition. Since it has been found, too, that the condition of a substance in dilute solution is at least nearly identical with that of the same substance in the form of vapor at the same temperature and pressure, examination of the behavior of such solutions has led to the perfecting of methods of molecular-weight determination for substances for which vapor-density methods were not readily available. All the results obtained, however, have had to do with substances in a state of vapor only, or in a condition practically identical with the gaseous state; the complexity of the molecules of liquids was unknown and no suitable method for its determination has, until recently, been proposed. It is intended in this short review to call attention to the results obtained in this field of research chiefly by Prof. W. Ramsay, of London.

Eötvös, in 1886,² had called attention to the fact that the rate of change of the surface-energy of a liquid with respect to the temperature is an approximately constant one, or, in other words, $\frac{d\gamma s}{dt} = k$, where γ = surface-tension, s = surface, and t =

¹ *Loc. cit.*

² *Ann. der Phys. Wied.*, **27**, 448 (1886).

temperature measured downward from the critical temperature. The reasoning upon which Eötvös based his deductions from experimental results was, however, at fault.¹ One suggestion that he made has nevertheless proved of great value: in order to make his formula apply to all liquids he makes s = the molecular surface, *i. e.*, that surface over which, whatever the liquid, the same number of molecules are distributed. He assumes that this surface $= (Mv)^{2/3}$, where Mv = the molecular volume of the liquid in question under the conditions of the experiment, *i. e.*, that volume which, whatever the liquid, contains the same number of molecules. If we imagine this volume a cube, then any edge would be represented by $(Mv)^{1/3}$, and any face by $(Mv)^{2/3}$. Assuming this value for s , Eötvös' formula becomes $\gamma(Mv)^{2/3} = k(T - T')$, where T is the critical temperature and T' that of the experiment.

Ostwald,² in his *Lehrbuch*, commenting upon the work of Eötvös, expresses the hope that this colligative property of liquids may serve for the determination of the molecular weights of substances in the liquid state.

The first paper by Ramsay and Shields³ describes an elaborate series of experiments undertaken in the hope of establishing the existence of a law connecting the critical temperature of a liquid and some one of the properties peculiar to the liquid state, in the same way that the volume-energy law of gases, $p v = RT$, connects the absolute temperature and the volume of a gas.

In the formula $p v = RT$, if v be constant, p decreases with T ; when $p = 0$, $T = -273^\circ$. Therefore, the origin of the scale of temperature is the origin of the scale of pressure. Correspondingly, in Eötvös' formula $\gamma s = K\tau$ (where τ is used to represent $T - T'$ or the number of degrees below the critical temperature at which the experiment is conducted), if s be constant, γ decreases with τ until $\gamma = 0$ when $\tau = 0$, or when the critical temperature is reached. Therefore, the origin of the scale of temperature is the origin of the scale of tension. Assuming, therefore, with Eötvös, that the molecular surface s may be regarded as equal to the molecular volume, Mv , raised to the two-thirds power, they have tested the formula $\gamma(Mv)^{2/3} = K\tau$ by making determinations of the rise of liquids in capillary tubes at temperatures ranging from -89.8° to the critical temperatures of the liquids.

The liquids examined were ether, methyl alcohol, ethyl

¹ Ramsay and Shields: Phil. Trans. 184, A, 660, (1893).

² 2nd. Ed., pp. 1129 and 1130.

³ Phil. Trans. 184, A, 647, (1893); also Ztschr. phys. Chem., 12, 433, (1893).

alcohol, methyl formate, ethyl acetate, carbon tetrachloride, benzene, chlorbenzene, and acetic acid. The data made use of were for the most part those determined by Ramsay and Young.¹

The apparatus consisted essentially of a capillary tube whose bore was accurately known at a certain point at which the level of the liquid within was always made to stand, enclosed in a sealed glass tube of large bore which contained nothing except the pure liquid and its vapor. The differences between the levels in the capillary and in the outer tube were measured by means of a cathetometer; correction being made at the same time for the capillary rise in the outer tube. The apparatus was so arranged that the level in the capillary always stood at the same point when measurements were being made; this avoided errors due to the varying size of the capillary tube. The outer tube was surrounded by a jacket filled with the vapor of some pure liquid whose boiling-points under various pressures were accurately known; by means of a mercury-gauge, the pressure under which the liquid boiled could be varied so as to obtain any desired temperature for the jacket. With this apparatus, experiments were made for each of the nine liquids mentioned, at intervals of 10° for the most part, from 20° to the critical temperature. In the case of ether, methyl formate, and ethyl acetate, experiments were also made at -89.8°, the tube being surrounded with boiling nitrous oxide.²

The results show that the formula $\gamma(Mv)^{\frac{2}{3}} = K\tau$ does not express the truth, but that for ether, methyl formate, ethyl acetate, carbon tetrachloride, benzene, and chlorbenzene, the formula $\gamma(Mv)^{\frac{2}{3}} = K(\tau - d)$, where d is a small number—averaging about 5°,—expresses with accuracy the variation of the surface-energy with the temperature to within 20°–30° of the critical temperature. Thus, in a drawing where the ordinates represent temperatures, and the abscissæ surface-energies, the “curve” representing the change of surface-energy with temperature is a straight line to within a few degrees of the critical temperature. The surface-tension was calculated by means of the formula $\gamma = \frac{1}{2}rhg(\rho - \sigma)$, where r = radius of capillary tube, h = capillary rise, g = gravitation-constant, ρ = density of the liquid at the temperature of

¹For ether, methyl alcohol, and ethyl alcohol, see Ramsay, and Young: *Phil. Trans.*, **178**, A, 57, 313, (1887); **177**, A, 123, (1886). For methyl formate, and ethyl acetate, see Young and Thomas: *J. Chem. Soc.* **63**, 1191, (1893); for carbon tetrachloride, see Young: *Ibid.* **59**, 932, (1891); for benzene, same: *Ibid.* **55**, 504, (1889); **59**, 134, (1891); for chlorbenzene, same: *Ibid.* **59**, 134; for acetic acid, see Ramsay and Young: *Ibid.* **49**, 790, (1886); Young: *Ibid.* **59**, 909, (1891).

²See *J. Chem. Soc.*, **63**, 833, (1893).

the experiment, and σ = density of the vapor at the same temperature.

On the other hand, the results obtained with methyl alcohol, ethyl alcohol, and acetic acid, do not agree with the formula: K is not a constant but varies between comparatively wide limits. In order that K may be a constant with a value between 2.04 and 2.22—as was found in the case of the liquids obeying the law—it must be assumed that the value of $\gamma(Mv)^{\frac{2}{3}}$ does not vary regularly with the temperature. Since γ and v are determined in each case by experiment, the conclusion is drawn that M , in these cases, varies according to the temperature, or, in other words, the molecules of these three liquids are more complex at low than at high temperatures. The relative degree of complexity was calculated as follows: Assuming that the molecular weights of the "non-associating" liquids are the same as their molecular weights in the gaseous state, then we must multiply the "gaseous" molecular weights of "associating" liquids by some factor x to obtain the relative weights of their liquid molecules; x will, of course, vary with the temperature. For acetic acid, then, the equation would become $\gamma(xMv)^{\frac{2}{3}} = K(\tau - d)$, M being taken as 60. Assuming for K the value 2.12, the average of the values found for the six non-associating liquids, and using k to denote the value found for the "constant" at any given temperature, the value of x for that temperature was found from the equation $x^{\frac{2}{3}} = \frac{K}{k}$. Thus, at

20° the values of x for acetic acid, methyl alcohol, and ethyl alcohol were found, respectively, to be 3.73, 3.43, and 2.79. As will be shown later, this method of calculating x is not quite correct and gives too high values.

There are many facts known which go to show that the molecular weights of certain liquids vary with change of temperature. Thus Beckmann¹ showed by freezing-point determinations that acetic acid and ethyl alcohol possess more complex molecules in concentrated solution than in the vapor state, whereas the molecular weight of naphthalene does not increase under similar conditions. Cundall² has shown that solutions of nitrogen peroxide behave in such a way as to show that the molecules of the oxide are more complex in solution, than in the gaseous state, at the same temperature and

¹ Ztschr. phys. Chem., **2**, 728, (1888.) Parizek and Sule conclude from their experiments [Ber. d. chem. Ges., **26**, 1408, (1893)] that water, ethyl alcohol, and the acids of the formic-acid series associate at low temperatures, but that the ethereal salts do not.

² J. Chem. Soc., **59**, 1076, (1891).

pressure. Ramsay and Young¹ have also shown that the density of acetic-acid vapor rises as the boiling-point is approached. But for a thorough treatment of this question the reader is referred to the papers of Guye² and of Ramsay³; the main features of these may be stated in a few words as follows:

(1) Guye has shown⁴ that the critical coefficient—*i. e.*, the quotient obtained by dividing the absolute critical temperature by the critical pressure—is equal to the molecular refraction multiplied by a constant with a value of about 1.8. While for most liquids this law holds, the constant for water, methyl alcohol and acetic acid has a value about 1.1, indicating association.

(2) Young and Thomas have shown⁵ that the densities of liquids at their critical points may be found by multiplying their theoretical densities by the constant 3.85. The constants in the cases of methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid are found, however, to be 4.52, 4.02, 4.02, and 5.00, respectively—indicating association.

(3) Young and Thomas have also shown that the method suggested by Cailletet and Matthias for finding the true volume of a liquid at its critical point, while applicable to most liquids, leads to anomalous results in the cases of water, methyl, ethyl, and propyl alcohols, and acetic acid. An explanation of these results is readily found if we assume association for all five substances when in the liquid state, and for the last, acetic acid, in the state of vapor also.

(4.) The heat of vaporization of a liquid diminishes regularly with rise of temperature until the critical temperature is reached, when its value is zero. The total heat absorbed may, however, in the case of a liquid which dissociates with rise of temperature, rise to a maximum and then decrease, owing to the conversion of more complex into simpler molecules. This is found by Ramsay and Young to be the case with ethyl alcohol and acetic acid.

(5.) The vapor-pressure curves of non-dissociating liquids do not cut one another at any point in their course, whereas the curves of dissociating liquids often cut those of normal liquids and at times those of other dissociating liquids. From these curves, then, the fact of the existence of complex molecules in a liquid can be proved.

¹ Phil. Mag., **24**, 196, (1887).

² Arch. Sci. phys. nat. Gen., [3], **31**, 38, 164.

³ Proc. Roy. Soc., **56**, 171, (1894); Ztschr. phys. Chem., **15**, 106.

⁴ Ann. chim. phys. [6] **21**, 206, 211; Arch. Sci. phys. nat. Gen., [3], **23**, 197.

⁵ J. Chem. Soc., **63**, 1251, (1893); also Phil. Mag., **34**, 507, (1892).

(6.) In van der Waal's vapor-pressure equation

$$\log pc - \log p = f \frac{T_c - T}{T},$$

—where pc and T_c are the critical pressure and temperature, respectively, and p some other pressure to a temperature T ,—the constant f has a value closely approximating 3 for all normal liquids. From Young's data for some sixteen liquids the average value is 3.06. Yet for associating liquids f is not constant and its value is higher. Thus its range is 3.56–3.77 for methyl alcohol, 3.58–4.02 for ethyl alcohol, 3.49–3.77 for propyl alcohol, 3.36–3.49 for acetic acid, and 3.20–3.24 for water.

(7.) The ratios of the volumes of saturated vapor at some chosen pressure to that at the critical pressure, as shown by Young,¹ points to association in the case of the acids and the alcohols.

(8.) The same fact is indicated by the greater values, in the case of water and the alcohols, of the heat of vaporization for unit increase of volume.²

(9.) Again, in the case of the alcohols, acetic acid, and water, the ratios of total to external work produced on evaporation are higher, showing greater internal work due to dissociation.

Having therefore shown that the connection between surface-energy and molecular weight exists as indicated in the formula $\gamma(Mv)^{\frac{2}{3}} = K(\tau - d)$ through at least a long range of temperature, Ramsay and Shields³ have made determinations of the surface-energies of a large number of liquids at a comparatively small number of points. The rate of change of the surface-energy with temperature could in this way be found with comparatively little labor. The apparatus was somewhat simplified; the density of the liquid was determined in a jacket of the same vapor as that used for heating the tube containing the capillary; as the temperatures of experiment were low the density of the vapor of the liquid (σ) was omitted in the equation $\gamma = \frac{1}{2} r h g (\rho - \sigma)$. It was found on comparing the data found for certain liquids by the original and by the simplified method that the error of experiment might be as much as 5 per cent.

The following liquids were found to give normal values for K and hence do not associate: Carbon bisulphide, nitrogen

¹ J. Chem. Soc., **63**, 1257 (1893).

² See Ramsay and Young: Proc. Phys. Soc., **7**, 303 (1885).

³ J. Chem. Soc., **63**, 1089 (1893).

peroxide,¹ silicon tetrachloride, phosphorus trichloride, phosphorus oxychloride, sulphur dichloride (S_2Cl_2), thionyl chloride ($SOCl_2$), sulphuryl chloride (SO_2Cl_2), nickel tetracarbonyl, normal octane, carbon tetrachloride, ethyl iodide, ethyl mercaptan, ethyl ether, chloral, paraldehyde, methyl formate, ethyl chlorformate, ethyl acetate, acetacetic ether, acetyl chloride, acetic anhydride, ethyl sulphocyanate, ethyl mustard-oil, allyl mustard-oil, benzene, chlorbenzene, benzaldehyde, nitrobenzene, aniline, phenyl cyanide, guaiacol, pyridine, piperidine, quinoline, and methylpropyl ketone.

The following substances have higher molecular weight in the liquid than in the gaseous state: Methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl and allyl alcohols; glycol; formic, acetic, propionic, butyric, isobutyric, valeric, and isocaproic acids; acetone; ethyl cyanide, nitroethane; water, and phenol.²

The writers find that it is possible, from the data found, to calculate with comparative accuracy the critical temperatures of the liquids examined.

Later determinations by Ramsay and Emily Aston³ have added to the list of associating substances, bromine, nitric and sulphuric acids. Liquid phosphorus seems to consist of molecules of the formula P_4 . It is of interest to note that a constant and very high molecular weight is found for sulphuric acid between 10° and 132° ; it then falls rapidly with rise of temperature. The authors call attention, in this connection, to the facts that complex sulphates, such as $NaK_5(SO_4)_3$, are well known, and that the acid has practically no vapor-pressure at ordinary temperatures.⁴ The true boiling-point, they therefore conclude, is very much higher than 360° , which is only the point of dissociation under atmospheric pressure.

In order still further to test the accuracy of the formula and the constancy of the value of K for normal liquids, the original method was applied in the determination of the surface-energies of eight more ethereal salts, certain necessary data for which had been recently published by Young.⁵ The salts used were ethyl formate, methyl acetate, propyl formate, methyl propionate, propyl acetate, ethyl propionate, methyl butyrate, and methyl isobutyrate, and the specimens employed were those originally used by Young. Determinations of surface-

¹ Of course nitrogen peroxide is known to associate in the gaseous state.

² For data for phenol, see J. Chem. Soc., **65**, 168 (1894).

³ *Ibid.*, 167.

⁴ Johnson [Chem. News, **68**, 211 (1893)] found that no sulphate is formed on leaving caustic soda in a desiccator over sulphuric acid for a month, nor was the liquid alloy of potassium and sodium affected under the same conditions; whereas gold-leaf left for the same period over mercury was heavily amalgamated.

⁵ J. Chem. Soc., **63**, 1191 (1893).

tension¹ were made at seven or eight points ranging from 10° to 210°–240°. The value of K ranged from 2.042 for methyl formate, to 2.248 for methyl isobutyrate, increasing with the complexity of the acid radicle.

It seems, therefore, to be established that within wide limits of temperature, the molecular surface-energy of non-associating compounds is a linear function of the temperature. Fourteen such substances have been examined at temperatures ranging from, in certain cases, –89.8° to within a few degrees of the critical temperature, while thirty others have been shown to accord with the law within more restricted limits of temperature. The question now rises, is it fair to assume that for normal liquids the molecular weight in the liquid and gaseous states is the same? When Ramsay and Shields assumed in their earlier work that it was, there was no positive evidence in favor of such a view; there was just as much reason for assuming that the liquid molecules are formed by the union of two, three, or more, gaseous molecules, so far as any experimental data bearing on the question are concerned. Nor was there any physical connection manifest between the equations for the volume-energy of gases and the surface-energy of liquids; their similarity was a mere coincidence. Within the past year, however, van der Waals has published a paper² on the thermodynamic theory of capillarity, in which is given a formula for calculating γ , based on purely theoretical grounds, by the application of which the value of γ for ether at –89.8° is found,³ on calculation, to be identical with the (hitherto unpublished) value found by Ramsay and Shields.

But on other grounds there is much to be said in favor of the assumption. One thing is certain: If, in the case of normal liquids, gaseous molecules unite with one another to form liquid molecules, they all associate to an equal extent, and the degree of association is not altered by rise of temperature. These two assertions are probably not true: it is unlikely that mere liquifaction should produce, in all cases, equal association; and it is unlikely that a rise of temperature should not cause the dissociation of an associated body. Change from the gaseous to the liquid state may be regarded as essentially equivalent to increase of pressure, since each produces approach between the molecules, diminishing intermolecular distance, and bringing so-called molecular forces into play. Now it is well known that equal rise of pressure does not

¹ Proc. Roy. Soc., **56**, 162 (1894); Ztschr. phys. Chem., **15**, 98.

² Ztschr. phys. Chem., **13**, 657 (1894).

³ Proc. Roy. Soc., **56**, 181 (1894); Ztschr. phys. Chem., **15**, 115.

always produce equal increment of association; hence it is unlikely that association to an equal extent should be caused by the reduction of the volumes of compounds until they are approximately equal.¹

In determining the average molecular weights in the case of associating liquids, it was assumed that there would be a distribution of the simpler and more complex molecules over the capillary surface proportional to the relative quantities of these molecules in the body of the liquid. This assumption has been tested² and, in so far as it affects the rate of change of surface-energy, has been found to be justified. Experiments were made with mixtures of (*a*) toluene and piperidine (5:1; 1:5), (*b*) benzene and carbon tetrachloride (1:1; 10:17; 2:1), (*c*) chlor-benzene and ethylene bromide (1:1), and (*d*) chloroform and carbon bisulphide (1:1). The results show that, at least in certain cases, the molecular surface-energy of a mixture is the mean of those of its constituents determined at the same temperature. Further experiments in this direction are now in progress.

Returning³ finally to the matter of determining the actual molecular weights of associating liquids, Ramsay has pointed out an error in the former work, due to the assumption that the value of x could be determined without taking into account the variation of $x^{2/3}$ with the temperature. More careful examination has shown, however, that this factor must be taken into account. As a result of this examination a formula was deduced which agrees with the results found and avoids the error referred to. The value of x has been thus recalculated for the following liquids:

	Temperature-range.	Range of x .
Methyl alcohol	—89.8°–220°	2.65 –1.75
Ethyl alcohol	—89.8°–230°	2.03 –1.00
Water	0°–140°	1.707–1.289
Acetic acid	20°–280°	2.13 –1.30

A recent paper⁴ by Guye gives the results obtained by applying still another method to the determination of the molecular weights of liquid hydrocarbons. Making use of the data given by Landolt and Jahn,⁵ and by Altschul,⁶ he calculates the ratio between the molecular refraction and the critical co-

¹ Proc. Roy. Soc., **56**, 166–7 (1894); Ztschr. phys. Chem., **15**, 103.

² Proc. Roy. Soc., **56**, 182; Ztschr. phys. Chem., **15**, 89.

³ Proc. Roy. Soc., **56**, 175; Ztschr. phys. Chem., **15**, 111.

⁴ Bull. Soc. chim., (Paris), [3], **13**, 34, (1895).

⁵ Ztschr. phys. Chem., **10**, 289, (1892).

⁶ *Ibid.* **11**, 577, (1893).

efficient, and so determines¹ the molecular weight at the critical point. Since, following Ramsay's reasoning, it is more likely that the molecular weights in the liquid and gaseous states are identical than that the substances examined should all associate on liquefaction to just the same extent, he decides that the molecular weight in the gaseous state and that at the critical point are identical. The liquids examined were: pentane, hexane, octane, decane, benzene, toluene, ethylbenzene, the three xylenes, propylbenzene, isopropylbenzene, mesitylene, pseudocumene, isobutylbenzene, and cymene.

The identity of the molecular weights at the critical point and in the gaseous state, is also proved by a comparison of the critical coefficient found for any given substance, and that calculated from the atomic coefficients of the elements which compose it. K_c calculated ranges from 13.8 to 22.8; K_c found, from 13.6 to 21.5, for the substances named, "double-bonds" being supposed absent in the aromatic ring. Assuming the presence of double bonds, the figures found do not coincide so well.

Applying now the method of van der Waals,² the identity of the molecular weights of these hydrocarbons in the *liquid* state and at the critical point was demonstrated.

WYATT W. RANDALL.

OBITUARY NOTICES.

JAMES D. DANA.

Though Professor Dana was not a chemist, there are special reasons for noticing his death in this place. The first of these is his position among the scientific men of this country. His untiring devotion to science in the highest sense has served as an inspiration to many who were not working in the same fields, and the effect will continue to be felt. Again, the fact that, notwithstanding his great age, he never gave up work, is one that should be taken to heart by younger men in the hours and days when the sense of weariness comes upon them.

Up to the year 1878 the present writer had sent his chemical articles to the "American Journal of Science and Arts," and they had been kindly received. In the year named, however, a number of articles were sent in together and, in the course of a few days, they were returned with a long and extremely

¹ See §(1), p. 465.

² See §(6), p. 466.

friendly letter from Professor Dana, in which he made it clear that he could not publish the articles without entirely changing the character of his journal; and, at the same time, he strongly urged the starting of a chemical journal. The letter led to correspondence which resulted in the foundation of this Journal, the first number of which appeared in April, 1879. The editor of the new journal was entirely inexperienced in the work that devolved upon him, and he owes much to the wise counsel and friendly coöperation of Professor Dana.

I. R.

LOTHAR MEYER.

By the death of Lothar Meyer, chemistry loses one of her most philosophical disciples, one whose writings have helped the cause of clear thinking probably as much as those of any other chemist of the last twenty-five years.

Lothar Meyer was born August 19, 1830, at Varel in Oldenburg. He first studied medicine and for a time carried on work in physiology. In 1858 he established himself as *Privat-docent* in the University of Breslau, and became, later, Director of the chemical laboratory. In 1866 he was appointed Professor of Natural Science in the Forestry Academy, at Neustadt-Eberswalde, near Berlin. In 1868 he accepted a call, as Professor of chemistry, to the Polytechnic Institute, at Carlsruhe, and in 1876 he went to Tübingen, where he filled the professorship of chemistry until his death, which occurred April 22.

Meyer was one of the first chemists in Germany to appreciate the full significance of Avogadro's hypothesis. In a note to his edition of Cannizzaro's "*Abriss eines Lehrganges der Theoretischen Chemie*,"¹ there is an exceedingly interesting account of an attempt made in 1860, by some of the leading chemists, to bring order out of the chaos of chemical thought then prevailing. Meyer was present at the celebrated Carlsruhe convention, and was much impressed by the speech of Cannizzaro. He confesses that "the scales fell from his eyes, and his doubts disappeared, and a feeling of quiet certainty took its place." This experience led him, a few years later, to prepare his well-known "*Die Modernen Theorien der Chemie*," which appeared in 1864. It was not especially well received at first, but as years passed it exerted a more and more powerful influence on the thoughts of chemists. From a flimsy pamphlet it grew to a stately volume, and it has generally been recognized as the best presentation of the fundamental principles of chemistry until the physicochemical movement began.

¹ Ostwald's *Classiker der exakten Wissenschaften*. No. 30. Engelmann, Leipzig.

Meyer's name will always be remembered in connection with the Periodic Law. The evidence seems to be conclusive that he recognized the law independently of Mendeléeff and at the same time; and he has since done much to bring out clearly the remarkable relations which exist between the atomic weights of the elements.

As indicated at the beginning of this notice, it was as a chemical philosopher rather than as an experimental investigator, that Meyer gained eminence, though some of his experimental work is of high order.

I. R.

GERHARD KRÜSS.

Gerhard Krüss, Ausserordentlicher Professor of Chemistry in the University of Munich, and founder and Editor of the "*Zeitschrift für anorganische Chemie*," died in Munich, Feb. 3, aged 36. Krüss began the study of chemistry in 1879 at Munich, and, excepting a summer with Bunsen in Heidelberg and a winter with Nilson in Stockholm, he remained in Munich as student, assistant, privatdocent, and professor until his death. Krüss was a rapid and accurate worker, and a man of unflagging industry and energy. Between 1882 and the present year, he published sixty-nine articles embodying the results of his own work, and that of his pupils. Among his more important investigations are those on the sulphur derivatives of molybdenum, on the atomic weight of gold, on the double sulphocyanates of iron, on the vanadium sulphides of chromium, on beryllium, on various rare earths. Krüss was a skillful spectroscopist. In 1891 he published with his brother, Hugo Krüss, a book entitled "*Colorimetry and Quantitative Spectrum Analysis*," which is of high value and was favorably received. In 1892 he published his manual of "*Special Analytic Methods*," a second edition of which was printed in the following year. Krüss wrote the articles on inorganic chemistry in Richard Meyer's "*Jahrbuch der Chemie*," in the years 1892, 1893, 1894. In 1892 Krüss founded the "*Zeitschrift für anorganische Chemie*." The science of inorganic chemistry loses in Gerhard Krüss an indefatigable worker, and a teacher who knew how to inspire his pupils with his own enthusiasm.

E. R.

AMERICAN CHEMICAL JOURNAL.

SOME NOTES ON MOLECULAR AND ATOMIC REFRACTION.

BY W. F. EDWARDS.

In a paper¹ read at the Brooklyn meeting of the American Association for the Advancement of Science, I offered a new formula, $\frac{P(M-1)}{MD}$, for molecular refraction, and gave examples to show that the formula was sufficiently concordant with experiment to warrant further investigation. It was also shown that in the cases of five alcohols, five aldehydes, six acids, and seven ethereal salts, the numbers representing the difference of molecular refraction for a difference of CH_2 in the molecular formula were in favor of the formula $\frac{P(M-1)}{MD}$ when compared with the formula $\frac{P(M^2-1)}{(M^2+2)D}$ the difference between the extreme values being 1.70 per cent. of the mean value in the case of the former, and 2.82 per cent. of the mean value in the case of the latter.

In this paper a number of examples were given to show that the difference in the molecular refraction for a difference of CH_2 in the molecular formula was greater when an acid was compared with an ethereal salt, than when a series of like

¹ This JOURNAL, 16, 625.

compounds, such as alcohols, aldehydes, acids, etc., were compared. In the present paper this comparison is extended to twenty-one cases of acids and ethereal salts and confirms the result obtained before for the formula $\frac{P(M-1)}{MD}$, but gives a doubtful result as regards the Lorentz-Lorenz formula.

The chief purpose of the present paper is to give a somewhat extended comparison of the three formulæ, $\frac{P(M-1)}{D}$, $\frac{P(M-1)}{(M^2+2)D}$, and $\frac{P(M-1)}{MD}$, and to determine numbers for the atomic refractions of carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, iodine, and sulphur, for the last formula, more especial attention being given to the determination of numbers for the first four elements mentioned.

In table I which follows—divisions *A* (hydrocarbons), *B* (alcohols), *C* (aldehydes), *D* (acids), *E* (ethereal salts), *F* (nitrogen compounds), and *G* (sulphur compounds)—the indices of refraction are given for sodium light. The molecular refractions and differences for CH_2 are, therefore, for sodium light.

Several considerations have led me to give these numbers for sodium light. Among them may be mentioned: (1) the ease with which sodium light can be obtained in any laboratory; (2) sodium light can be used with any refractometer; (3) some instruments, like that after Abbé, have a compensating device by the use of which sunlight may be used for obtaining the indices of refraction for sodium light; (4) the indices of refraction of gases are more generally given for sodium light; (5) many laboratories have polariscopes of the Laurent type, and with it some contrivance for obtaining a suitable sodium light. It seems to me that if we have numbers for sodium light there will be a more general comparison possible and a more general determination of molecular refraction for the reasons before stated.

As an example of greater possibility of comparison may be cited the hydrocarbons from octane to hexadecane in division *A* of table I. So far as I know the indices of refraction of these hydrocarbons have not been given for any other than

sodium light as found in the paper of Bartoli and Stracciati.¹ These investigators obtained their hydrocarbons by painstaking fractionation of American petroleum, and, while the portions used distilled at an approximately constant temperature, they cannot, of course, be considered as pure. It will be noticed, indeed, that the temperature of ebullition was about 10° below that given for corresponding hydrocarbons by Krafft.²

It is much to be regretted that Krafft did not supplement his excellent work by a more extended determination of the physical properties. It is also to be regretted that Bartoli and Stracciati, after finding the temperature of ebullition, do not state the pressure, and, after finding the density at 0° C. and the coefficients α and β of the formula $D_t = D_0 (1 - \alpha t - \beta t^2)$; the coefficients of expansion between 0° and 30° C. and between 0° and the temperature of ebullition; the molecular volume at the temperature of ebullition; the specific heat; the constants of capillary action; the electrical properties; and the indices of refraction for sodium light, did not determine the indices of refraction for at least light of one other color so that some idea of the dispersive power of the substances could be obtained. The day has gone by when the chemist can ignore the physical properties of the substances with which he works. It may be said, also, that the physicist cannot ignore the chemical constitutions of the substances with which he works. The ultimate aims of the physicist and the chemist are, alike, the determination, as nearly as may be, of the very nature of matter itself. If the chemist has not the means of determining the physical constants of new compounds—or old ones, for that matter—his compound should be turned over to the physicist who should be glad of an opportunity to add to the record of physical constants. The chemist should be held by a similar bond to aid the physicist. This co-operative way of working would leave no excuse for the omission of the physical properties of a substance whether the discoverer be a chemist or a physicist.

¹ Ann. chim. phys., [6] **7**, 375-383 (1886).

² Ber. d. chem. Ges., **15**, 1687, 1711.

The headings of the column in table I are, in general, a sufficient explanation of the numbers in those columns. Perhaps, however, it is desirable to call attention to the columns headed "difference for CH_2 ," for the purpose of explaining the cases where there are two differences given. In division *E* we have ethyl acetate with differences 6.81 and 6.96, in the first column headed "differences for CH_2 ." In this case the number for ethyl acetate has been compared with that of methyl acetate and that of ethyl formate. The same explanation applies to the second and third columns headed "difference for CH_2 ." In divisions *H*, *I*, *J*, and *K*, *M* is given for red hydrogen light.

In calculating the number for molecular refraction, wherever the specific gravity or index of refraction has been given to the fifth decimal, the fifth decimal has been omitted if less than 5, and where 5 or more than 5, 1 has been added to the fourth decimal figure. The specific refraction has been determined to the fourth decimal place before multiplying by the molecular weight. The third decimal of the molecular refraction has been omitted when under 5; when 5 or more, 1 has been added to the second decimal figure.

Where *M* is calculated it is by means of Cauchy's dispersion-formula as given in Landolt and Börnstein's *Tabellen*.

If we consider x as the greatest error in the numbers representing molecular refraction, the number for pentane, division *A*, first column headed molecular refraction, would be $41.26 \pm x$ and for hexadecane it would be $126.33 \pm x$. Assume that it is $-x$ in the first case and $+x$ in the second case, then the difference for CH_2 is $(126.33 + x) - (41.26 - x)$ divided by eleven, the number of times CH_2 must be added to the pentane molecule to make the hexadecane molecule. This gives an average difference from pentane to hexadecane of $7.73 + 2/11 x$ and is correct to within some quantity not greater than $\frac{2x}{11}$. The differences for CH_2 in division *A* show

that each CH_2 added to the pentane molecule adds an approximately equal increment to the numbers standing for the molecular refraction. If the number found in this way be averaged with the mean difference of division *A*, we have :

$$7.73 + 7.76 \div 2 = 7.74.$$

TABLE I.

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at t_0 .	Index of refraction for ray D.	Molecular refraction $\frac{P(M-1)}{D}$.	Difference for CH_2 .	Molecular refraction $\frac{P(M-1)}{D}$.	Difference for CH_2 .	Molecular refraction $\frac{P(M-1)}{D}$.	Difference for CH_2 .	From the data of	Remarks.
<i>A: Hydrocarbons.</i>													
Isopentane	C_5H_{12}	72.0	6.5°	0.6365	1.3649	41.26		25.27		30.24		Gladstone.	B. P. 30°.
" (P)	C_5H_{12}	"	16.	0.6174	1.3583	41.76		25.85		30.74		"	" 68°.
Hexane	C_6H_{14}	86.0	16.	0.6765	1.3851	49.11	7.85	29.84	4.57	35.36	5.12	"	" 48°-52°.
"	C_6H_{14}	"	25.	0.6317	1.3602	49.03	7.77	30.01	4.16	36.04	5.80	Gladstone.	" 92°-94°.
Heptane	C_7H_{16}	100.0	16.	0.7144	1.4037	56.04	6.93	34.20	4.36	40.25	4.89	Bartoli and Stracciati.	
"	"	"	7.6	0.6935	1.3945	59.90	7.87	34.53	4.69	40.79	5.43	Gladstone.	
"	"	"	12.	0.6895	1.3917	56.81	7.78	34.51	4.67	40.82	5.46	"	
"	"	"	23.	0.6809	1.3867	56.89	7.86	34.55	4.71	40.95	5.59	"	
Octane	C_8H_{18}	114.0	16.	0.7290	1.4202	64.40	8.36	38.92	4.72	45.62	5.37	Bartoli and Stracciati.	B. P. 116°-118°.
Nonane	C_9H_{20}	128.0	"	0.7457	1.4273	72.19	7.79	43.39	4.37	50.82	5.20	"	" 136°-138°.
Decane	$\text{C}_{10}\text{H}_{22}$	142.0	"	0.7561	1.4254	79.95	7.76	48.08	4.69	56.07	5.25	"	" 158°-162°.
Undecane	$\text{C}_{11}\text{H}_{24}$	156.0	"	0.7673	1.4316	87.67	7.72	52.62	4.54	61.27	5.20	"	" 180°-182°.
Dodecane	$\text{C}_{12}\text{H}_{26}$	170.0	"	0.7769	1.4367	96.54	7.87	57.29	4.67	66.52	5.25	"	" 198°-200°.
Tridecane	$\text{C}_{13}\text{H}_{28}$	184.0	"	0.7881	1.4422	103.22	7.68	61.81	4.52	71.95	5.13	"	" 218°-220°.
Tetradecane	$\text{C}_{14}\text{H}_{30}$	198.0	"	0.7948	1.4489	111.67	8.45	66.71	4.90	77.08	5.13	"	" 236°-240°.
Pentadecane	$\text{C}_{15}\text{H}_{32}$	212.0	"	0.8096	1.4531	118.51	6.81	70.79	4.08	81.86	4.78	"	" 258°-262°.
Hexadecane	$\text{C}_{16}\text{H}_{34}$	226.0	"	0.8167	1.4567	126.33	7.82	75.37	4.58	86.78	4.92	"	" 278°-282°.
Mean..							7.76		4.56		5.26		
Benzene	C_6H_6	78.0	10.	0.8903	1.5978	44.48		26.11		29.50		Gladstone.	
"	C_6H_6	"	20.	0.8799	1.5914	44.41		26.14		29.60		Brühl.	
Toluene	C_7H_8	92.0	7.5	0.8704	1.4982	52.76	8.28	30.99	4.88	35.22	5.72	Gladstone.	
"	C_7H_8	"	20.	0.8656	1.4955	52.66	8.22	31.05	4.91	35.21	5.61	Brühl.	
<i>o</i> -Xylene	C_8H_{10}	106.0	18.	0.8632	1.4966	60.98	8.22	35.90	4.91	40.75	5.53	Gladstone.	
"	"	"	15.5	0.8726	1.5020	60.98	8.22	35.85	4.86	40.60	5.38	"	
<i>p</i> -Xylene	"	"	16.	0.8488	1.4846	60.52	7.76	35.75	4.76	40.76	5.34	Brühl.	
Mesitylene	C_9H_{12}	120.0	20.	0.8558	1.4912	68.87	8.35	40.60	4.85	46.19	5.43	Gladstone.	B. P. 175°-176°.
Cumene	C_9H_{12}	"	12.	0.8432	1.4801	68.33	7.81	40.43	4.68	46.16	5.40	Brühl.	
Cymene	$\text{C}_{10}\text{H}_{14}$	134.0	22.6	0.8530	1.4847	74.16	7.81	45.00	4.57	51.28	5.12	"	
Mean..							8.08		4.80		5.47		

TABLE I.—Continued.

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t/4$.	Index of refraction for ray D.	Molecular refraction, $\frac{D}{M-1}$	Difference for CH_2 .	Molecular refraction, $\frac{P(M-1)}{M+2}$	Difference for CH_2 .	Molecular refraction, $\frac{MD}{M-1}$	Difference for CH_2 .	From the data of	Remarks.
<i>B: Alcohols.</i>													
Methyl	CH_4O	32.0	18.0°	0.7961	1.3301	13.27		8.14		9.94		Gladstone.	
Ethyl	$\text{C}_2\text{H}_6\text{O}$	46.0	20.	0.7887	1.36164	21.09	7.82	12.92	4.78	15.49	5.55	Ketteler.	
Propyl	$\text{C}_3\text{H}_8\text{O}$	60.0	"	0.8044	1.39543	28.75	7.66	17.35	4.43	20.75	5.26	Brühl.	
Isopropyl	$\text{C}_3\text{H}_8\text{O}$	60.0	"	0.7887	1.37757	28.72	7.63	17.53	4.61	20.85	5.36	"	
Butyl	$\text{C}_4\text{H}_{10}\text{O}$	74.0	"	0.8099	1.3991	36.47	7.72	22.10	4.57	26.06	5.31	"	
Isobutyl	$\text{C}_4\text{H}_{10}\text{O}$	74.0	"	0.8062	1.3959	36.34	7.62	22.04	4.51	26.03	5.18	Landolt.	
Isoamyl	$\text{C}_5\text{H}_{12}\text{O}$	88.0	"	0.8123	1.4078	44.18	7.84	26.69	4.65	31.38	5.35	"	
Phenol	$\text{C}_6\text{H}_6\text{O}$	94.0	21.	1.0595	1.5509	48.86	28.28	28.28		31.49	5.04	Gladstone.	
Cresol	$\text{C}_7\text{H}_8\text{O}$	108.0	23.	1.0390	1.5419	56.32	7.46	32.46	4.18	36.53	5.01	"	
m-Cresol	$\text{C}_7\text{H}_8\text{O}$	108.0	19.	1.0330	1.5364	56.08	7.22	32.63	4.35	36.50	5.26	"	
					Mean..		7.62		4.51				
<i>C: Aldehydes.</i>													
Acetic	$\text{C}_2\text{H}_4\text{O}$	44.0	20.0°	0.7799	1.3316	18.71		11.56		14.05		Landolt.	<i>M</i> calculated.
Propionic	$\text{C}_3\text{H}_6\text{O}$	58.0	"	0.8066	1.3636	26.15	7.44	16.01	4.45	19.17	5.17	Brühl.	
Butyric	$\text{C}_4\text{H}_8\text{O}$	72.0	"	0.8170	1.3843	33.87	7.72	20.62	4.61	24.47	5.30	"	
Isobutyric	$\text{C}_4\text{H}_8\text{O}$	72.0	"	0.7938	1.3730	33.83	7.68	21.36	5.35	24.63	5.46	"	
Valeric	$\text{C}_5\text{H}_{10}\text{O}$	86.0	"	0.7984	1.3882	41.80	7.98	25.43	4.07	30.12	5.49	Landolt.	<i>M</i> calculated.
Heptonic	$\text{C}_7\text{H}_{14}\text{O}$	114.0	"	0.8495	1.4257	57.13	7.66	34.36	4.47	40.08	4.98	Brühl.	
					Mean..		7.70		4.59		5.27		
<i>D: Acids.</i>													
Formic	CH_2O_2	46.0	20.0°	1.2188	1.3714	14.02		8.57		10.22		Landolt.	<i>M</i> calculated.
Acetic	$\text{C}_2\text{H}_4\text{O}_2$	60.0	"	1.0495	1.3718	21.26	7.24	12.98	4.41	15.49	5.27	"	"
Propionic	$\text{C}_3\text{H}_6\text{O}_2$	74.0	"	0.9446	1.3866	28.76	7.50	17.49	4.51	20.74	5.25	"	"
Butyric	$\text{C}_4\text{H}_8\text{O}_2$	88.0	"	0.9587	1.3979	36.52	7.76	22.47	4.98	26.12	5.38	Brühl.	
Isobutyric	$\text{C}_4\text{H}_8\text{O}_2$	88.0	"	0.9490	1.3930	36.44	7.68	22.13	4.64	26.03	5.29	"	
Isovaleric	$\text{C}_5\text{H}_{10}\text{O}_2$	102.0	"	0.9295	1.4043	44.36	7.92	26.85	4.72	31.52	5.49	Landolt.	<i>M</i> calculated.
Isocaproic	$\text{C}_6\text{H}_{12}\text{O}_2$	116.0	"	0.9237	1.4138	51.96	7.66	31.37	4.52	36.74	5.22	"	"
Heptonic	$\text{C}_7\text{H}_{14}\text{O}_2$	130.0	"	0.9160	1.4215	59.81	7.85	36.02	4.65	42.08	5.34	"	"
					Mean..		7.67		4.63		5.32		

TABLE I.—Continued.

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t/4^\circ$.	Index of refraction for ray D.	Molecular refraction, $\frac{D}{P(M-1)}$	Difference for CH_2 .	Molecular refraction, $\frac{P(M-1)}{D}$	Difference for CH_2 .	Molecular refraction, $\frac{MD}{P(M-1)}$	Difference for CH_2 .	From the data of	Remarks.
Methyl formate.....	$\text{C}_2\text{H}_4\text{O}_2$	60.0	20.0°	0.9694	1.3438	21.28	8.10	13.07	4.94	15.83	5.57	J. H. Long.	B. P. 32.8° (P. 735 mm.) M calculated.
Ethyl "	$\text{C}_3\text{H}_6\text{O}_2$	74.0	"	0.9664	1.3599	29.38	7.67	18.01	4.60	21.60	5.31	Landolt.	B. P. 67° (P. 431 mm.) " 99° (P. 735 mm.) M calculated.
Propyl "	$\text{C}_4\text{H}_8\text{O}_2$	88.0	"	0.8662	1.3775	37.07	8.57	22.67	5.09	32.82	5.91	J. H. Long.	"
Isobutyl "	$\text{C}_4\text{H}_{10}\text{O}_2$	102.0	"	0.8657	1.3874	45.64	6.68	27.70	4.33	37.42	4.60	Landolt.	"
Amyl "	$\text{C}_5\text{H}_{12}\text{O}_2$	116.0	"	0.8832	1.3980	52.32	8.25	32.03	5.02	46.00	4.78	"	"
Methyl acetate.....	$\text{C}_3\text{H}_6\text{O}_2$	74.0	"	0.9039	1.3010	29.53	6.81	18.09	4.23	21.69	4.87	"	"
Ethyl "	$\text{C}_4\text{H}_8\text{O}_2$	88.0	"	0.9007	1.3726	36.34	6.96	22.24	4.71	26.47	5.50	Brühl.	B. P. 100°.
Propyl "	$\text{C}_5\text{H}_{10}\text{O}_2$	102.0	"	0.8856	1.3844	44.27	7.93	26.91	4.30	31.97	5.06	"	" 114° (P. 735 mm.) M calculated.
Ethyl butyrate.....	$\text{C}_6\text{H}_{12}\text{O}_2$	116.0	"	0.8906	1.3960	51.50	7.23	31.30	3.60	36.89	4.97	J. H. Long.	"
Amyl acetate.....	$\text{C}_7\text{H}_{14}\text{O}_2$	130.0	"	0.8561	1.4038	61.36	9.86	37.12	5.82	43.71	6.82	Landolt.	"
Methyl propionate..	$\text{C}_4\text{H}_8\text{O}_2$	88.0	"	0.9246	1.3776	35.94	6.41	21.92	5.09	26.09	6.29	J. H. Long.	B. P. 79.5° (P. 735 mm.) " 81.5° (P. 402 mm.) " 101.5° (P. 384 mm.) " 135.5° (P. 735 mm.) " 159.5° (") " 103.5° (") " 90.0° (") " 114.0° (") " 107.0° (") " 130.5° (")
Ethyl " ..	$\text{C}_5\text{H}_{10}\text{O}_2$	102.0	"	0.8904	1.3842	44.01	8.97	26.57	4.65	31.79	5.70	"	"
Propyl " ..	$\text{C}_6\text{H}_{12}\text{O}_2$	116.0	"	0.8828	1.3935	51.71	7.70	31.30	4.73	37.11	5.32	"	"
Isobutyl " ..	$\text{C}_7\text{H}_{14}\text{O}_2$	130.0	"	0.8694	1.3975	59.43	7.72	36.05	4.75	42.53	5.41	"	"
Amyl " ..	$\text{C}_8\text{H}_{16}\text{O}_2$	144.0	"	0.8703	1.4065	67.27	7.84	40.80	4.75	47.79	5.26	"	"
Methyl butyrate ...	$\text{C}_5\text{H}_{10}\text{O}_2$	102.0	"	0.8976	1.3889	44.17	8.23	26.87	4.95	31.80	5.71	"	"
" isobutyrate..	"	"	"	0.8893	1.3840	44.01	7.83	26.58	4.63	31.82	5.33	"	"
Ethyl butyrate.....	$\text{C}_6\text{H}_{12}\text{O}_2$	116.0	"	0.8906	1.3960	51.50	8.10	26.58	4.63	31.82	5.73	"	"
" isobutyrate..	"	"	"	0.8697	1.3880	51.75	7.70	31.30	4.34	36.89	5.35	"	"
Propyl " ..	$\text{C}_7\text{H}_{14}\text{O}_2$	130.0	"	0.8738	1.3959	58.90	7.49	31.47	4.73	37.29	5.10	"	"
							7.50	35.71	4.60	42.19	5.49	"	"
							7.45	5.24	4.41	4.96	5.30	"	"

TABLE I.—Continued.

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t^{\circ}/4$.	Index of refraction for ray D.	Molecular refraction, $\frac{D}{P(M-1)}$	Difference for CH_2 .	Molecular refraction, $\frac{(M+2)D}{P(M-1)}$	Difference for CH_2 .	Molecular refraction, $\frac{PM(-1)}{M^2-1}$	Difference for CH_2 .	From the data of	Remarks.
Isobutyl butyrate	$\text{C}_9\text{H}_{18}\text{O}_2$	144.0	20.0°	0.8627	1.4045	67.52	8.62	40.87	5.16	48.07	5.88	J. H. Long.	B. P. 154.5° (P. 735 mm.)
Isobutyl isobutyrate	"	"	"	0.8575	1.3999	67.16	8.19	40.69	4.82	47.99	5.84	"	" 144.5° (")
Amyl butyrate.....	$\text{C}_9\text{H}_{18}\text{O}_2$	158.0	"	0.8646	1.4110	75.11	7.77	46.72	4.98	53.23	5.86	"	" 178.° (")
Amyl isobutyrate....	"	"	"	0.8580	1.4076	75.06	7.95	44.45	5.85	53.32	5.24	"	" 166.5° (")
Methyl valerate	$\text{C}_6\text{H}_{12}\text{O}_2$	116.0	"	0.8795	1.3948	51.97	7.91	31.60	3.76	37.26	5.33	Landolt.	<i>M</i> calculated.
Ethyl "	$\text{C}_7\text{H}_{14}\text{O}_2$	130.0	"	0.8661	1.3971	59.54	7.80	36.15	3.58	42.61	5.44	"	"
Propyl "	$\text{C}_8\text{H}_{16}\text{O}_2$	144.0	"	0.8634	1.4036	67.32	7.57	40.75	4.55	47.96	5.72	J. H. Long.	B. P. 156.° (P. 735 mm.)
Isobutyl "	$\text{C}_9\text{H}_{18}\text{O}_2$	158.0	"	0.8558	1.4063	75.01	7.78	45.39	4.85	53.34	5.77	"	" 169.° (")
Amyl "	$\text{C}_{10}\text{H}_{20}\text{O}_2$	172.0	"	0.8568	1.4120	82.73	7.69	49.95	4.64	58.59	5.27	Landolt.	<i>M</i> calculated.
						Mean...	7.62		4.56		5.36		
							7.68		4.62		5.33		

Halogen Derivatives.

Propyl chloride	$\text{C}_3\text{H}_7\text{Cl}$	78.5	20.0°	0.8898	1.3886	34.28	8.39	20.84	4.58	24.66	5.83	Brühl.	<i>M</i> calculated.
Isobutyl "	$\text{C}_4\text{H}_9\text{Cl}$	92.5	19.0°	0.8626	1.3979	42.67	7.31	25.87	5.03	30.52	5.24	Gladstone.	
Amyl "	$\text{C}_5\text{H}_{11}\text{Cl}$	106.5	20.0°	0.8740	1.4102	49.68	7.31	30.17	4.30	35.44	4.92	Jahn.	
Ethyl bromide.....	$\text{C}_2\text{H}_5\text{Br}$	109.0	"	1.4555	1.4239	31.74	7.74	19.48	4.58	22.20	5.25	Weegmann.	<i>M</i> calculated.
Ethyl "	"	"	"	1.4569	1.4241	31.73	7.74	19.10	4.58	22.28	5.25	Haagen.	
Propyl "	$\text{C}_3\text{H}_7\text{Br}$	123.0	"	1.3520	1.4339	39.47	7.73	23.68	4.58	27.53	5.25	Brühl.	
Isopropyl "	"	"	"	1.3097	1.4251	39.93	8.20	24.02	4.92	28.01	5.73	"	
Isoamyl "	$\text{C}_5\text{H}_{11}\text{Br}$	151.0	"	1.2202	1.4412	55.42	8.19	33.17	4.54	38.45	5.22	Haagen.	<i>M</i> calculated.
Methyl iodide.....	CH_3I	142.0	"	2.2582	1.5297	33.30	7.98	19.41	4.74	21.77	5.46	"	
Ethyl "	$\text{C}_2\text{H}_5\text{I}$	156.0	"	1.9395	1.5131	41.46	8.16	27.40	4.89	27.40	5.63	"	
Propyl "	$\text{C}_3\text{H}_7\text{I}$	170.0	"	1.7427	1.5051	49.16	7.70	28.93	4.63	32.66	5.26	Brühl.	<i>M</i> calculated.
Isopropyl "	"	"	"	1.7033	1.4997	49.86	8.40	29.34	5.04	33.25	5.85	"	
Butyl "	$\text{C}_4\text{H}_9\text{I}$	184.0	"	1.6166	1.5001	56.91	7.75	33.47	4.54	37.94	5.28	"	
Isobutyl "	"	"	"	1.6056	1.4960	56.78	6.92	33.47	4.13	37.99	4.74	Gladstone.	
Amyl "	$\text{C}_5\text{H}_{11}\text{I}$	198.0	14.0°	1.5048	1.4960	65.26	8.48	38.43	4.96	43.62	5.63	"	
						Mean ..	7.90		4.64		5.41		

TABLE I.—Continued.

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t/4^\circ$.	Index of refraction for ray D.	Molecular refraction, $\frac{D}{P(M-1)}$	Difference for CH_2 .	Molecular refraction, $\frac{P(M-1)}{(M+2)D}$	Difference for CH_2 .	Molecular refraction, $\frac{MD}{P(M-1)}$	Difference for CH_2 .	From the data of	Remarks.
<i>F: Nitrogen Compounds.</i>													
Propyl amine.....	$\text{C}_3\text{H}_9\text{N}$	59.0	23.5°	0.7140	1.3873	32.00	7.84	19.46	4.78	23.07	5.65	Gladstone.	
Diethyl ".....	$\text{C}_4\text{H}_{11}\text{N}$	73.0	19.0°	0.7092	1.3871	39.84	7.84	24.24	4.78	28.72	5.38	"	
Triethyl ".....	$\text{C}_6\text{H}_{15}\text{N}$	101.0	"	0.7317	1.4005	35.28	7.72	33.49	4.63	39.47	5.35	"	<i>M</i> calculated.
Dipropyl ".....	$\text{C}_6\text{H}_{15}\text{N}$	"	23.2°	0.7356	1.4025	55.27	7.72	33.46	4.61	39.42	5.71	"	
Tripropyl ".....	$\text{C}_9\text{H}_{21}\text{N}$	143.0	22.8°	0.7535	1.4171	80.15	8.29	47.71	4.75	56.56	5.32	"	
Aniline.....	$\text{C}_6\text{H}_7\text{N}$	93.0	13.0°	1.0160	1.5828	53.34	8.04	30.58	4.71	33.70	5.12	Brühl.	
<i>o</i> -Toluidine.....	$\text{C}_7\text{H}_9\text{N}$	107.0	20.0°	0.9986	1.5128	61.38	8.04	35.29	4.71	39.02	4.92	Gladstone.	
Xylidine.....	$\text{C}_8\text{H}_{11}\text{N}$	121.0	19.0°	0.9867	1.5585	68.49	7.11	39.55	4.26	43.94	5.12	"	
Propionitrile.....	$\text{C}_3\text{H}_5\text{N}$	55.0	"	0.7862	1.3681	25.75	7.42	15.76	4.45	18.92	5.84	"	
Valeronitrile.....	$\text{C}_5\text{H}_9\text{N}$	83.0	18.0°	0.8010	1.3917	40.59	7.42	24.65	4.45	29.16	5.41	"	
Capronitrile.....	$\text{C}_6\text{H}_{11}\text{N}$	97.0	"	0.8040	1.4087	49.31	8.72	29.81	4.67	35.00	5.41	"	
<i>G: Sulphur Compounds.</i>													
Ethyl mercaptan.....	$\text{C}_2\text{H}_6\text{S}$	62.0	20.0°	0.8031	1.4366	29.89	8.67	17.96	5.17	20.89	5.93	Nasini.	
Isobutyl ".....	$\text{C}_4\text{H}_{10}\text{S}$	90.0	"	0.8357	1.4386	47.23	7.73	28.30	4.61	32.76	5.62	"	
Isaamyl ".....	$\text{C}_5\text{H}_{12}\text{S}$	104.0	"	0.8348	1.4412	54.96	7.39	32.91	4.44	38.38	5.40	"	
Ethyl sulphide.....	$\text{C}_2\text{H}_6\text{S}_2$	90.0	"	0.8368	1.4423	47.57	7.39	28.47	4.54	32.98	5.21	"	
Amyl ".....	$\text{C}_{10}\text{H}_{22}\text{S}$	174.0	"	0.8431	1.4524	93.37	7.03	55.71	4.69	64.28	5.54	"	
<i>H: Alcohols. (Ray Hα.)</i>													
Water.....	H_2O	18.0	20.0°	0.99824	1.3355	5.96	7.23	3.69	4.47	4.48	5.45	Brühl.	
Methyl alcohol.....	CH_3O	32.0	"	0.7953	1.32789	13.19	7.54	8.16	4.55	9.93	5.30	"	
Ethyl ".....	$\text{C}_2\text{H}_5\text{O}$	46.0	"	0.8000	1.36054	20.73	7.83	12.71	4.73	15.23	5.44	"	
Propyl ".....	$\text{C}_3\text{H}_7\text{O}$	60.0	"	0.8044	1.38345	28.56	7.61	17.42	4.73	20.67	5.31	"	
Isopropyl ".....	$\text{C}_3\text{H}_8\text{O}$	"	"	0.8039	1.37938	28.34	7.71	17.44	4.59	20.54	5.29	"	
Butyl ".....	$\text{C}_4\text{H}_9\text{O}$	74.0	"	0.8099	1.39712	36.27	7.82	22.01	4.52	25.96	5.40	"	
Isobutyl ".....	"	"	"	0.8062	1.39395	36.16	7.74	21.96	4.71	25.94	5.60	"	
Trimethyl carbinol..	"	"	"	0.7864	1.38572	36.30	7.74	22.13	4.61	26.27	5.30	"	
Amyl alcohol.....	$\text{C}_5\text{H}_{12}\text{O}$	88.0	"	0.8123	1.40573	43.95	7.79	26.62	4.43	31.26	5.26	"	
Methylhexylcarbinol	$\text{C}_8\text{H}_{18}\text{O}$	130.0	"	0.8193	1.42231	67.01	7.66	40.35	4.59	47.06	5.37	"	

TABLE I.—Continued.

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t^{\circ}/4$.	Index of refraction for ray H α .	Molecular refraction, $\frac{D}{P(M-1)}$	Difference for CH $_2$.	Molecular refraction, $\frac{D}{P(M-1)}$	Difference for CH $_2$.	Molecular refraction, $\frac{D}{P(M-1)}$	Difference for CH $_2$.	From the data of	Remarks.
<i>I: Aldehydes.</i>													
Acetic.....	C $_2$ H $_4$ O	44.0	20.0°	0.7799	1.32975	18.61		11.50		13.99		Brühl.	
Propionic.....	C $_3$ H $_6$ O	58.0	"	0.8066	1.36157	26.00	7.39	15.93	4.43	19.10	5.11	"	
Butyric.....	C $_4$ H $_8$ O	72.0	"	0.8170	1.38222	33.68	7.65	20.52	4.59	24.36	5.26	"	
Isobutyric.....	C $_4$ H $_8$ O	72.0	"	0.7938	1.37094	33.64	7.64	20.56	4.63	24.46	5.36	"	
Valeric.....	C $_5$ H $_{10}$ O	86.0	"	0.7984	1.38614	41.60	7.96	25.31	4.75	29.99	5.63	"	
Heptylic.....	C $_7$ H $_{14}$ O	114.0	"	0.8495	1.42340	56.82	7.61	34.20	4.45	39.91	4.96	"	
					Mean..		7.66		4.57		5.26		
<i>J: Acids.</i>													
Formic.....	CH $_2$ O $_2$	46.0	20.0°	1.2188	1.36927	13.94		8.52		10.28		Brühl.	
Acetic.....	C $_2$ H $_4$ O $_2$	60.0	"	1.0495	1.36985	21.55	7.61	12.93	4.41	15.44	5.16	"	
Propionic.....	C $_3$ H $_6$ O $_2$	74.0	"	0.9946	1.38460	28.02	7.07	17.42	4.49	20.66	5.22	"	
Butyric.....	C $_4$ H $_8$ O $_2$	88.0	"	0.9594	1.39554	36.28	7.66	22.01	4.59	25.99	5.33	"	
Isobutyric.....	C $_4$ H $_8$ O $_2$	88.0	"	0.9490	1.39093	36.25	7.63	22.03	4.61	26.06	5.40	"	
Isovaleric.....	C $_5$ H $_{10}$ O $_2$	102.0	"	0.9298	1.40220	44.12	7.87	26.72	4.69	31.45	5.39	"	
Isocaproic.....	C $_6$ H $_{12}$ O $_2$	116.0	"	0.9237	1.41164	51.70	7.58	31.22	4.50	36.62	5.17	"	
Heptic.....	C $_7$ H $_{14}$ O $_2$	130.0	"	0.9160	1.41923	59.50	7.80	35.85	4.63	41.92	5.30	"	
					Mean.		7.60		4.56		5.28		
<i>K: Ethereal Salts.</i>													
Ethyl formate.....	C $_3$ H $_6$ O $_2$	74.0	20.0°	0.9064	1.35800	29.23		17.93		21.52		Brühl.	
Ethyl acetate.....	C $_4$ H $_8$ O $_2$	88.0	"	0.9007	1.37068	36.22	6.99	22.14	4.21	26.42	4.90	"	
Propyl ".....	C $_5$ H $_{10}$ O $_2$	102.0	"	0.8856	1.3824	44.04	7.82	26.83	4.69	31.86	5.44	"	
Ethyl butyrate.....	C $_6$ H $_{12}$ O $_2$	116.0	"	0.8892	1.39494	51.41	7.37	31.20	4.37	36.85	4.92	"	
Ethyl valerate.....	C $_7$ H $_{14}$ O $_2$	130.0	"	0.8861	1.39500	59.28	7.87	35.98	4.78	42.51	5.66	"	
Methyl acetate.....	C $_3$ H $_6$ O $_2$	74.0	"	0.9039	1.35915	29.41	7.47	18.03	4.49	21.63	5.22	"	
Ethyl ".....	C $_4$ H $_8$ O $_2$	88.0	"	0.9007	1.37068	36.22	6.81	22.14	4.11	26.42	4.79	"	
Propyl ".....	C $_5$ H $_{10}$ O $_2$	102.0	"	0.8856	1.3824	44.04	7.82	26.83	4.69	31.86	5.44	"	
Ethyl benzoate.....	C $_9$ H $_{10}$ O $_2$	150.0	"	1.0473	1.50104	71.76	7.69	42.20	4.65	47.80	5.44	Landolt.	
Methyl ".....	C $_8$ H $_8$ O $_2$	136.0	"	1.0862	1.51158	64.07		37.55		42.36		"	
					Mean..		7.48		4.50		5.24		

If each division of table I be treated similarly for each of the three formulæ we shall have average differences for CH_2 , as given in table II. (Division *G* is omitted.)

TABLE II.

Division.	For $\frac{P(M-1)}{D}$	For $\frac{P(M^2-1)}{D(M^2+2)}$	For $\frac{P(M-1)}{MD}$
<i>A</i> , paraffins	7.74	4.56	5.25
" aromatic	8.00	4.75	5.44
<i>B</i> , paraffins	7.68	4.62	5.28
" aromatic	7.48	4.45	5.14
<i>C</i> , paraffins	7.69	4.58	5.24
<i>D</i> , "	7.65	4.61	5.31
<i>E</i> , "	7.68	4.62	5.34
" chlorides	7.87	4.65	5.39
" bromides	7.89	4.60	5.39
" iodides	7.94	4.69	5.37
<i>F</i> , paraffins	8.15	4.69	5.50
" aromatic	7.72	4.58	5.27
" nitriles	7.85	4.68	5.36
Mean for sodium light.	7.77	4.62	5.33
<i>H</i> , paraffins	7.65	4.58	5.35
<i>I</i> , "	7.65	4.56	5.22
<i>J</i> , "	7.60	4.56	5.31
<i>K</i> "	7.50	4.51	5.25
Mean for red hydrogen light	7.60	4.55	5.28
Mean for the paraffins of <i>B</i> , <i>C</i> , <i>D</i> , and <i>E</i> . .	7.68	4.61	5.29

The comparison of the mean values for CH_2 of groups *H*, *I*, *J*, and *K*, with those of the like compound in groups *B*, *C*, *D*, and *E*, show higher numbers for sodium light in each case, but higher for the Gladstone and Lorentz-Lorenz formulæ than for the formula $\frac{P(M-1)}{MD}$. That this result is con-

sistent with the three formulæ will appear from a brief consideration of them.

Consider the Gladstone formula for the same substance at the same temperature. We have $(M-1)K$, where K is a constant equal to P/D ; let $M=1+x$, then $(M-1)K=Kx$, from which we determine that the molecular refraction varies with x .

In all ordinary cases x is greater for sodium light than for red hydrogen light. An inspection of the numbers in divisions H , I , J , and K , as compared with corresponding numbers in divisions B , C , D , and E of table I, shows that this is true in practice, as shown by the molecular refraction. We should then expect to find the differences for CH_2 to be a little greater for the paraffins of divisions B , C , D , and E , then for divisions H , I , J , and K of table I. An inspection of table II shows this to be the case.

If we consider the Lorentz-Lorenz formula in the same way we have $\frac{(1+x^2)-1}{(1+x^2)+2} K = K \frac{2+x}{2+x+3/x} = \frac{1}{1+\frac{3}{2x+x^2}} K$, which

shows that the molecular refraction is greater in the case of sodium light, where x is greater, than for red hydrogen light.

A comparison of the indices of refraction of like substances in divisions B and H and D and J show that x is about 0.002 more for sodium light than for red hydrogen light. This difference will affect $\frac{3}{2x+x^2}$ more in the case of the alcohols than in the case of the acids since x is smaller in the case of the alcohols.

From this table we have 4.58 for ray $\text{H}\alpha$ and 4.62 for ray D for the alcohols, and 4.56 for ray $\text{H}\alpha$ and 4.61 for ray D for the acids. This discrepancy is explained by the fact that there are more alcohols compared in group H than in group B .

In the same way we have for the formula $\frac{P(M-1)}{MD}$, $K \frac{x}{1+x} = K \frac{1}{1+\frac{1}{x}}$ which shows that the greater the value of x the

greater will be the molecular refraction, and the less the influence of the increment of 0.002 in the index of refraction.

DETERMINATION OF ATOMIC REFRACTION.

Carbon, Hydrogen, and Oxygen.

In the determination of the values for atomic refraction, the values 7.68 for the Gladstone formula, 4.61 for the Lorentz-Lorenz formula, 5.29 for the formula $\frac{P(M-1)}{MD}$ will be as-

sumed as representing the difference in the molecular refraction for a difference of CH_2 in the molecule. It will be observed that these numbers are the averages given in table II for the paraffins of groups *B*, *C*, and *D*, and the first division of group *E*.

The acids may be considered as $n(\text{CH}_2) + \text{carbonyl}$ and hydroxyl oxygen. If $n \times 7.68$ for the Gladstone formula, $n \times 4.61$ for the Lorentz-Lorenz formula, and $n \times 5.29$ for the formula $\frac{P(M-1)}{MD}$, be subtracted from the molecular refraction of the acids the difference will stand for the oxygen of the group $\text{O}=\text{C}\angle\text{O}-\text{H}$. Table III shows these differences and gives an average of 5.95 for the Gladstone formula, 3.81 for the Lorentz-Lorenz formula, and 4.97 for my formula.

The aldehydes may be considered as $n(\text{CH}_2) + \text{carbonyl}$ oxygen. If, then, $n \times 7.68$, $n \times 4.61$, and $n \times 5.29$ be subtracted from the numbers representing the corresponding molecular refractions of the aldehydes the difference will stand for carbonyl oxygen.

Table IV shows these differences and gives an average of 3.25 for the Gladstone, 2.35 for the Lorentz-Lorenz and 3.38 for my formula.

The difference between the numbers standing for oxygen of the group $\text{O}=\text{C}\angle\text{O}-\text{H}$ and that of the group $=\text{C}=\text{O}$ will stand for the oxygen of the group $\equiv\text{C}-\text{O}-\text{H}$. Making the subtraction we find 2.70 for the Gladstone formula, 1.46 for the Lorenz formula, and 1.59 for my formula.

The alcohols may be considered as $n(\text{CH}_2) + \text{hydroxyl}$ oxygen $+ 2\text{H}$. If, then, $n \times 7.68 + 2.70$, $n \times 4.61 + 1.46$, and $n \times 5.29 + 1.59$ be subtracted from the molecular refraction of the alcohols the difference will stand for 2H for the corresponding formula. Table V shows these differences and gives an average of 3.00 for the Gladstone formula, 2.16 for the Lorentz-Lorenz formula, and 3.28 for the formula $\frac{P(M-1)}{MD}$.

The values for hydrogen are, then, 1.50, 1.08, and 1.64, and, therefore, the values for carbon are $7.68 - 3.00 = 4.68$; $4.61 - 2.16 = 2.45$; and $5.29 - 3.28 = 2.01$; for the three formulæ in the order observed in the columns of the tables.

TABLE III.—*Acids.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{DM}$		
	Molecular refraction.	$n \times 7.68$.	Difference $_{2O}$.	Molecular refraction.	$n \times 4.61$.	Difference $_{2O}$.	Molecular refraction.	$n \times 5.29$.	Difference $_{2O}$.
Formic	14.02	7.68	6.34	8.57	4.61	3.96	10.22	5.29	4.93
Acetic	21.26	15.36	5.90	12.98	9.22	3.76	15.49	10.58	4.91
Propionic....	28.76	23.04	5.72	17.49	13.83	3.66	20.74	15.87	4.87
Butyric	36.52	30.72	5.80	22.47	18.44	4.03	26.12	21.16	4.96
Isovaleric....	44.36	38.40	5.96	26.85	23.05	3.80	31.52	26.45	5.07
Isocaproic ...	51.96	46.08	5.88	31.37	27.66	3.71	36.74	31.74	5.00
Heptoic.....	59.81	53.76	6.05	36.02	32.27	3.75	42.08	37.03	5.05
Mean			5.95			3.81			4.97

TABLE IV.—*Aldehydes.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.68$.	Difference $_O$.	Molecular refraction.	$n \times 4.61$.	Difference $_O$.	Molecular refraction.	$n \times 5.29$.	Difference $_O$.
Acetic	18.71	15.36	3.35	11.56	9.22	2.34	14.05	10.58	3.47
Propionic....	26.15	23.04	3.11	16.01	13.82	2.18	19.17	15.87	3.30
Butyric	33.87	30.72	3.15	20.62	18.44	2.18	24.47	21.16	3.31
Isobutyric....	33.83	"	3.11	21.36	18.44	2.92	24.63	21.16	3.47
Valeric	41.81	38.40	2.41	25.43	23.05	2.38	30.12	26.45	3.67
Heptoic.....	57.13	53.76	3.37	34.36	32.27	2.09	40.08	37.03	3.05
Mean			3.25			2.35			3.38

TABLE V.—*Alcohols.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$N(7.68) + 2.70$.	Difference $_{2H}$.	Molecular refraction.	$N(4.61) + 1.46$.	Difference $_{2H}$.	Molecular refraction.	$N(5.29) + 1.59$.	Difference $_{2H}$.
Methyl	13.27	10.38	2.89	8.14	6.07	2.07	9.94	6.88	3.06
Ethyl.....	21.09	18.06	3.03	12.92	10.68	2.24	15.49	12.17	3.32
Propyl.....	28.75	25.74	3.01	17.35	15.29	2.06	20.75	17.46	3.29
Isopropyl....	28.72	"	2.98	17.53	"	2.24	20.85	"	3.39
Butyl.....	36.47	33.42	3.05	22.10	19.90	2.20	26.06	22.75	3.31
Isobutyl.....	36.34	"	2.92	22.04	"	2.14	26.03	"	3.28
Isoamyl	44.18	41.10	3.08	26.69	24.51	2.18	31.38	28.04	3.34
Mean			3.00			2.16			3.28

I desire to call attention to the close approximation of the separate differences for $_{2O}$ in table III to the mean for each

of the formulæ. A like comparison in the cases of O and 2H of tables IV and V is also desirable.

It has probably already been noted by the reader that the number obtained for hydrogen for the Gladstone formula is considerably larger than has been found for that element heretofore, and that the number for carbon is considerably less than has been found for that element. The number found by subtracting $n \times 7.68$ from the molecular refraction of the hydrocarbons of division A of table I is a number somewhat higher even than this. These numbers appear in table VI.

TABLE VI.—Hydrocarbons.

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.68$.	Difference 2H.	Molecular refraction.	$n \times 4.61$.	Difference 2H.	Molecular refraction.	$n \times 5.29$.	Difference 2H.
Pentane	41.26	38.40	2.86	25.27	23.05	2.22	30.24	26.45	3.79
"	41.76	"	3.36	25.85	"	2.80	30.74	"	4.29
Hexane.....	49.11	46.08	3.03	29.84	27.66	2.18	35.36	31.74	3.62
"	49.03	"	2.95	30.01	"	2.35	36.04	"	4.30
Heptane	56.04	53.76	2.28	34.20	32.27	1.93	40.22	37.03	3.19
"	56.90	"	3.14	34.53	"	2.26	40.79	"	3.76
"	56.81	"	3.05	34.51	"	2.24	40.82	"	3.79
"	56.89	"	3.13	34.55	"	2.28	40.95	"	3.92
Octane	64.40	61.44	2.96	38.92	36.88	2.14	45.62	42.32	3.30
Nonane	72.19	69.12	3.07	43.39	41.49	1.90	50.82	47.61	3.21
Decane	79.99	76.80	3.15	48.08	46.10	1.98	56.07	52.90	3.17
Undecane....	87.67	84.48	3.19	52.62	50.71	1.91	61.27	58.19	3.08
Dodecane....	95.54	92.16	3.38	57.29	55.32	1.97	66.52	63.48	3.04
Tridecane ..	103.78	99.84	3.84	61.81	59.93	1.88	71.95	68.77	3.23
Tetradecane	111.67	107.52	4.15	66.71	64.54	2.17	77.08	74.06	3.02
Pentadecane	118.51	115.20	3.31	70.79	69.15	1.64	81.86	79.35	5.51
Hexadecane	126.33	122.88	3.45	75.37	73.76	1.61	86.78	84.64	2.14
Mean		3.20			2.08				3.37

This table shows 1.60, 1.04, and 1.68 for hydrogen; and 4.48, 2.53, and 1.92 for carbon, for the three formulæ, the numbers being in the order of the arrangements observed in the tables. It was pointed out near the beginning of the paper that these hydrocarbons could not be considered pure, and I, therefore, do not rely on the numbers obtained for hydrogen and carbon from table VI, but use them to show that the numbers obtained from the oxygen compounds agree very well with those obtained from the hydrocarbons themselves. If these hydrocarbons were pure, then I should have

depended on these numbers and should have used them in determining hydroxyl oxygen instead of using hydroxyl oxygen to obtain numbers for hydrogen.

Before making closer comparisons I wish to make a comparison similar to that of tables III, IV, and V, using numbers obtained from the use of red hydrogen light. In this comparison the numbers 7.60, 4.55, and 5.28 will be used as representing CH_2 for the three formulæ in the usual order. It will be observed that they are the average differences for CH_2 in groups *H*, *I*, *J*, and *K* of table I, as shown in table II.

These comparisons are shown in tables VII, VIII, and IX.

TABLE VII.—*Acids.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.60.$	Difference $_{20}.$	Molecular refraction.	$n \times 4.55.$	Difference $_{20}.$	Molecular refraction.	$n \times 5.28.$	Difference $_{20}.$
Formic ...	13.94	7.60	6.34	8.52	4.55	3.97	10.28	5.28	5.00
Acetic	21.55	15.20	6.35	12.93	9.10	3.83	15.44	10.56	4.88
Propionic..	28.62	22.80	5.82	17.42	13.65	3.77	20.66	15.84	4.82
Butyric...	36.28	30.40	5.88	22.01	18.20	3.81	25.99	21.12	4.87
Isobutyric	36.25	"	5.85	22.03	"	3.83	26.06	"	4.94
Isovaleric.	44.12	38.00	6.12	26.72	22.75	3.97	31.45	26.40	5.05
Isocaproic	51.70	45.60	6.10	31.22	27.30	3.92	36.62	31.68	4.94
Heptonic ..	59.50	53.20	6.30	35.85	31.85	4.00	41.92	36.96	4.96
Mean			6.09			3.89			4.93

TABLE VIII.—*Aldehydes.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.60.$	Difference $_{20}.$	Molecular refraction.	$n \times 4.55.$	Difference $_{20}.$	Molecular refraction.	$n \times 5.28.$	Difference $_{20}.$
Acetic	18.61	15.20	3.41	11.50	9.10	2.40	13.99	10.56	3.44
Propionic..	26.00	22.80	3.20	15.73	13.65	2.26	19.10	15.84	3.26
Butyric ...	33.68	30.40	3.18	20.52	18.20	2.32	24.36	21.12	3.24
Isobutyric	33.63	"	3.24	20.56	"	2.34	24.46	"	3.34
Valeric ...	41.60	38.00	3.60	25.31	22.74	2.56	29.99	26.40	3.59
Heptonic...	56.80	53.20	3.60	34.20	31.85	2.35	39.91	36.96	2.95
			3.37			2.37			3.30

This shows 2.72, 1.52, and 1.63 for hydroxyl oxygen for the three formulæ taken in the usual order.

TABLE IX.—Alcohols.

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction. $n \times 7.60$ + 2.72.	Difference 2H.		Molecular refraction. $n \times 4.55$ + 1.52.	Difference 2H.		Molecular refraction. $n \times 5.28$ + 1.63.	Difference 2H.	
Methyl . . .	13.19	10.32	2.87	8.16	6.07	2.09	9.93	6.91	3.02
Ethyl	20.73	17.92	2.81	12.71	10.62	2.09	15.23	12.18	3.04
Propyl	28.56	25.52	3.04	17.42	15.17	2.25	20.67	17.47	3.20
Isopropyl . .	28.34	25.52	2.82	17.44	15.17	2.27	20.54	17.47	3.07
Butyl	36.27	33.12	3.15	22.01	19.72	2.29	25.96	22.75	3.21
Isobutyl . .	36.16	33.12	3.04	21.96	19.72	2.24	25.94	22.75	3.19
Amyl	43.95	40.72	3.23	26.62	24.27	2.35	31.26	28.03	3.23
Mean		2.99			2.22				3.28

From tables III, IV, and V, and tables VII, VIII, and IX, we have for the

	Carbon.	Hydrogen.	Carbonyl oxygen.	Hydroxyl oxygen.
Gladstone formula for sodium light	4.68	1.50	3.25	2.70
“ red hydrogen light	4.61	1.50	3.26	2.72
Lorentz-Lorenz formula for sodium “	2.45	1.08	2.35	1.46
“ red hydrogen light	2.33	1.11	2.37	1.52
Formula $\frac{P(M-1)}{MD}$ for sodium light	2.01	1.64	3.38	1.59
“ red hydrogen light	2.00	1.64	3.30	1.63

Ostwald, in the second edition of his *Lehrbuch der Allgemeinen Chemie*, pages 432–3, under investigations by Landolt, gives Landolt's numbers for carbon and hydrogen for the Gladstone formula in the following manner :

Substance.	Molecular refraction.	Difference C	Substance.	Molecular refraction.	Difference 2H.
Aldehyde	18.58	Ethyl alcohol	20.70
Methyl alcohol	13.24	5.44	Aldehyde	18.58	2.12
Acetone	26.12	Propyl alcohol	28.30
Ethyl alcohol	20.17	5.42	Acetone	26.12	2.18
Valeric aldehyde	41.54	Amyl alcohol	43.81
Butyl alcohol	36.11	5.43	Valeric aldehyde	41.54	2.35
Propionic acid	28.57	Ethylene alcohol	23.77
Ethylene alcohol	23.77	4.80	Acetic acid	21.11	2.66
Acetic anhydride	36.56	Glycerol	34.32
Lactic acid	31.81	4.75	Lactic acid	31.81	2.51

On page 433 he shows that if $n \times 7.60$ be subtracted from the molecular refraction of the acids, the mean difference is 6.00 which gives a mean value of 3.00 for oxygen. He then

obtains a mean value of 2.60 for $2H$ by subtracting $n \times 7.60 + 3.00$ from the molecular refraction of the alcohols. On pages 436-7, under investigations by Brühl, he shows that hydroxyl oxygen has one value, 2.75, and carbonyl oxygen another, 3.40, and gives in the table of atomic refractions carbonyl oxygen 3.40 and hydroxyl oxygen 2.80. If the number 2.75 instead of 3.00 had been used in finding a value for $2H$ from the alcohols, a value of 2.85 instead of 2.60 would have been found for $2H$, and of 4.75 instead of 5.00 for carbon.

It seems strange that this chance for a different value for hydrogen and therefore for carbon was not noticed by Ostwald and others, especially as Landolt, in the paper¹ abstracted by Ostwald, after giving the values 5.00 for carbon, 1.30 for hydrogen, and 3.00 for oxygen, calls attention to the close agreement of numbers obtained for carbon from diamond and for hydrogen and oxygen obtained from the gases. These numbers were 4.85 for carbon, 1.54 for hydrogen, and 3.04 for oxygen. This number for hydrogen is very close to the one found for hydrogen in this paper.

For the oxygen numbers found in this paper there is a difference between the values of hydroxyl and carbonyl oxygen of 0.55 for the Gladstone formula; of 0.89 for the Lorentz-Lorenz formula; and of 1.79 for my formula. For red hydrogen light there is a difference, in the same order, of 0.55, 0.85, and 1.67.

At the beginning of this paper I pointed out that there was a larger difference for the value of CH_2 obtained by comparing ethereal salts and acids than by comparing like compounds. I have since discovered Conrady's calculations² from which he obtains the following values for sodium light for the Lorentz-Lorenz formula: hydroxyl oxygen, 1.521; carbonyl oxygen, 2.87; ether oxygen, 1.683. The difference between 1.521 and 1.683 is too small a value to be of any practical use but agrees with the difference found by me in the paper before mentioned. Of course the figures of the third decimal place may be entirely ignored in all of Conrady's numbers.

Conrady in the same paper distinguishes carbon as carbon

¹ Pogg, Ann. der Phys., **123**, 623 (1864).

² Ztschr. phys. chem., **3**, 210 (1889).

standing alone, and carbon in combination with carbon. In the preceding tables methyl alcohol, formic acid, and methyl salts are examples of carbon standing alone. To carbon standing alone and designated by C° he gives the value 2.592, and to carbon in combination with carbon and designated by C' he gives the value 2.501 for sodium light.

Tables X and XI which follow show a decided difference between hydroxyl oxygen and ether oxygen for my formula, but do not for either of the others. Table XII shows that, on the average, carbon standing alone has a higher value than carbon in combination with carbon, but on the whole leaves the matter in a somewhat doubtful state.

TABLE X.—*Ethereal Salts.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.68.$	Difference $20.$	Molecular refraction.	$n \times 4.61.$	Difference $20.$	Molecular refraction.	$n \times 5.29.$	Difference $20.$
Ethyl formate	29.38	23.04	6.34	18.01	13.92	4.09	21.60	15.87	5.73
Propyl "	37.07	30.72	6.35	22.61	18.56	4.05	26.91	21.16	5.75
Amyl "	52.32	46.08	6.24	32.03	27.84	4.19	37.42	31.74	5.68
Methyl acetate . . .	28.53	23.04	6.49	18.09	13.92	4.17	21.69	15.87	5.82
Ethyl "	36.34	30.72	5.62	22.24	18.56	3.68	26.47	21.16	5.31
Propyl "	44.27	38.40	5.87	26.91	23.20	3.71	31.97	26.42	5.52
Methyl propionate .	35.94	30.72	5.22	21.92	18.56	3.36	26.09	21.16	4.93
Ethyl "	44.01	38.40	5.64	26.57	23.20	3.38	31.79	26.45	5.34
Amyl "	67.27	61.44	5.83	40.80	37.12	3.68	47.79	42.32	5.47
Methyl butyrate . .	44.04	38.40	5.64	26.58	23.20	3.38	31.82	26.45	5.37
Ethyl "	51.50	46.08	5.38	31.30	27.84	3.46	36.89	31.74	5.15
Amyl "	75.11	69.14	5.97	46.72	41.76	4.96	53.23	47.61	5.62
Methyl valerate . .	51.97	46.08	5.89	31.60	27.84	3.76	37.26	31.74	5.52
Ethyl "	59.54	53.76	5.78	36.15	32.48	3.67	42.61	37.03	5.58
Amyl "	82.73	76.80	5.93	49.95	46.50	3.45	58.59	52.90	5.69
Mean			5.88			3.78			5.50

The average 5.88 is only 0.07 below 5.95, the average difference of table III, and only five of the differences of table X are above 5.95. The average 3.78 is only 0.03 below that found in table III, and again only five of the differences of table X are above 3.81. The average 5.50 is 0.53 above 4.97, the average of table III, and with the exception of methyl propionate all the differences are above 4.97.

TABLE XI.

Substance.	$\frac{P(M-1)}{D}$	Diff. CH ₂ .	$\frac{P(M^2-1)}{D(M^2+2)}$	Diff. CH ₂ .	$\frac{P(M-1)}{MD}$	Diff. CH ₂ .
Methyl formate.....	21.28	13.07	15.83
Formic acid.....	14.02	7.26	8.57	4.50	10.22	5.61
Ethyl formate.....	29.38	18.01	21.60
Acetic acid.....	21.26	8.12	12.98	5.03	15.49	6.11
Propyl formate.....	37.07	22.61	26.91
Propionic acid	28.76	8.31	17.49	5.12	20.74	6.17
Isobutyl formate	45.64	27.70	32.82	6.79
Isobutyric acid	36.44	9.20	22.13	5.57	26.03
Amyl formate.....	52.32	32.03	37.42
Valeric acid	44.36	7.96	26.85	5.18	31.52	5.90
Methyl acetate.....	29.53	18.09	21.69
Acetic acid.....	21.26	8.27	12.98	5.11	15.49	6.20
Ethyl acetate.....	36.34	22.24	26.47
Propionic acid.....	28.76	7.58	17.49	4.75	20.74	5.63
Propyl acetate.....	44.27	26.91	31.97
Butyric acid.....	36.52	7.75	22.47	4.44	26.12	5.85
Methyl propionate.....	35.94	21.92	26.09
Propionic acid.....	28.76	7.18	17.49	4.43	20.74	5.35
Ethyl propionate.....	44.01	29.57	31.79
Butyric acid.....	36.52	7.49	22.47	4.10	26.12	5.67
Propyl propionate.....	51.71	31.30	37.11
Valeric acid.....	44.36	7.35	26.85	4.45	31.52	5.59
Isobutyl propionate.....	59.43	36.05	42.53
Caproic acid.....	51.96	7.47	31.37	4.68	36.74	5.79
Amyl propionate.....	67.27	40.80	47.79
Heptoic acid.....	59.81	7.46	36.02	4.78	42.08	5.71
Methyl butyrate.....	44.17	26.87	31.80
Butyric acid.....	36.52	7.65	22.47	4.40	26.12	5.68
Methyl isobutyrate.....	44.04	26.58	31.82
Isobutyric acid.....	36.44	7.60	22.13	4.45	26.03	5.79
Ethyl isobutyrate	51.75	31.47	37.28
Valeric acid.....	44.36	7.39	26.85	4.62	31.52	5.77
Propyl isobutyrate.....	58.90	35.71	42.19
Caproic acid.....	51.96	6.94	31.37	4.34	36.74	5.45
Isobutyl butyrate.....	67.52	40.87	48.07
Heptoic acid.....	59.81	7.71	36.02	4.85	42.08	5.99

Substance.	$\frac{P(M-1)}{D}$	Diff. CH ₂ .	$\frac{P(M^2-1)}{D(M^2+2)}$	Diff. CH ₂ .	$\frac{P(M-1)}{MD}$	Diff. CH ₂ .
Methyl valerate.....	51.97	31.60	37.26
Valeric acid.....	44.36	7.61	26.85	4.75	31.52	5.74
Ethyl valerate.....	59.54	36.15	42.61
Caproic acid.....	51.96	7.28	31.37	4.78	36.74	5.87
Propyl valerate.....	67.32	40.76	47.96
Heptic acid.....	59.81	7.51	36.02	4.73	42.08	5.88
Mean.....		7.68		4.72		5.84

In table XI the average difference for the Gladstone formula, 7.68, is the same as shown in table II. Fourteen of the twenty-one differences are below 7.68. The average difference for the Lorentz-Lorenz formula is 0.11 above 4.61; this agrees with Conrady's calculations very closely. Thirteen of the twenty-one differences are above 4.61, while only eight are below. The average difference for my formula is 0.55 above 5.29, and all the differences of the table are above 5.29. This agrees very closely with the number found in table X. For my formula, then, ether oxygen = $1.59 + 0.54 = 2.13$.

The first four differences of table X and the first six of table XI would seem to prove Conrady's proposition in regard to carbon standing alone. Both tables, however, contain a number of examples where it does not hold. Table XII also shows several examples where it does not hold, although more than half of the cases given in the table favor it.

The examples of table XII are taken from table I:

TABLE XII.

Substance.	$\frac{P(M-1)}{D}$	Diff. CH ₂ .	$\frac{P(M^2-1)}{D(M^2+2)}$	Diff. CH ₂ .	$\frac{P(M-1)}{MD}$	Diff. CH ₂ .
Ethyl formate.....	29.38	18.01	21.60
Ethyl acetate.....	36.34	6.96	22.24	4.23	26.47	4.87
Amyl formate.....	52.32	32.03	37.42
Amyl acetate.....	61.36	9.04	37.12	5.09	43.71	6.29
Methyl formate.....	21.28	13.07	15.83
Ethyl formate.....	29.38	8.10	18.01	4.94	21.60	5.77
Propyl formate.....	37.07	22.61	26.91
Propyl acetate.....	44.27	7.20	26.91	4.30	31.97	5.06

Substance.	$\frac{P(M-1)}{D}$	Diff. CH ₂ .	$\frac{P(M^2-1)}{D(M^2+2)}$	Diff. CH ₂ .	$\frac{P(M-1)}{MD}$	Diff. CH ₂ .
Isobutyl formate.....	45.64	27.70	32.82
Ethyl isobutyrate....	51.75	6.11	31.47	3.77	37.29	4.47
Methyl butyrate.....	44.17	26.87	31.80
Ethyl butyrate.....	51.50	7.33	30.30	4.43	36.89	5.09
Methyl isobutyrate..	44.04	26.58	31.82
Ethyl isobutyrate....	51.75	7.71	31.47	4.89	37.29	5.47
Methyl acetate.....	29.53	18.09	21.69
Ethyl "	36.44	6.81	22.24	4.15	26.47	4.78
Methyl propionate...	35.94	21.92	26.09
Ethyl " ...	44.01	8.67	26.57	4.65	31.79	5.70
Methyl valerate.....	51.97	31.60	37.26
Ethyl valerate.....	59.54	7.57	36.15	4.55	42.61	5.35
Methyl iodide.....	33.30	19.41	21.77
Ethyl "	41.46	8.16	24.30	4.89	27.40	5.63
Formic acid.....	14.02	8.57	10.22
Acetic "	21.26	7.24	12.98	4.41	15.49	5.27
Methyl alcohol.....	13.27	8.14	9.94
Ethyl "	21.09	<u>7.82</u>	12.94	<u>4.78</u>	15.49	<u>5.55</u>
Mean for sodium light..		7.56		4.55		5.33
Formic acid.....	13.94	8.53	10.28
Acetic "	21.55	7.61	12.93	4.41	15.44	5.16
Methyl alcohol.....	13.19	8.16	9.93
Ethyl "	20.73	7.54	12.71	4.55	15.23	5.30
Ethyl formate.....	29.23	17.93	21.53
Ethyl acetate.....	36.22	6.96	22.14	4.21	26.42	4.90
Methyl acetate.....	29.41	18.03	21.63
Ethyl "	36.22	6.81	22.14	4.11	26.42	4.79
Methyl benzoate.....	64.07	37.55	42.36
Ethyl "	71.76	<u>7.69</u>	42.20	<u>4.65</u>	47.80	<u>5.44</u>
		7.33		4.39		5.12

A careful inspection of the differences in table XII will show that we must have more evidence before accepting Conrady's "alleinstehenden Kohlenstoff" as having a different atomic-refraction value. In the last five examples, used for obtaining a value for red hydrogen light, the differences are about as much for as against Conrady's supposition, although

the average is decidedly in favor of it, for all three of the formulæ, and gives a greater difference than Conrady finds for the Lorentz-Lorenz formula.

Carbon United Ethylene-wise.

Carbon united ethylene-wise has a value for its atomic refraction very decidedly different from that found when the element is united in the ordinary way of the paraffins. Table XIII gives differences for a "double linking" in the column headed "difference for $1=$." In the column headed "Formula" I have designated the number of "double linkings" by " $1=$ " with a subscript figure which is the number assumed for that substance. In the case of furfural, I have assumed three ethylene-unions since it was the only way to make furfural a consistent substance for all of the formulæ. Its molecular refraction would indicate an alcohol and an aldehyde group, and three ethylene-unions of carbon. If considered as having two aldehyde groups it is consistent for my formula but not for the others.

I have aimed to give sufficiently variable examples in this table to show the value of atomic refraction in detecting the ethylene union.

It will be noticed that in the first division of this table there are several numbers differing widely from the general average. I do not offer any explanation. It may be due to experimental errors. In the case of the Gladstone and the Lorentz-Lorenz formulæ, it will be found that by using the numbers usually given for atomic refraction for those formulæ the widely differing differences are not made any nearer to the average. The differences in the second part of the table are very close to each other and to the average for all three formulæ. These averages will be assumed as correct in the calculations which appear in the tables which follow.

Nitrogen.

Gladstone¹ states that "nitrogen has two values, 4.1 and 5.1 or thereabouts." He also states that "the lower value is that which was originally assigned to it and seems to be gen-

¹ J. Chem. Soc., 45, 257.

TABLE XIII.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at $t/4^{\circ}$	Ind. n _D at $t/4^{\circ}$	$\frac{P(M-1)}{D}$		$\frac{P(M^2-1)}{(M^2+2)D}$		$\frac{P(M-1)}{MD}$		Data of
						Mol. refr.	Diff. $i =$	Mol. refr.	Diff. $i =$	Mol. refr.	Diff. $i =$	
Amylene	$C_6H_{10} I=$	70.0	20.0°	0.6476	1.3758	40.62	38.40	24.79	23.05	29.38	26.45	Brühl.
Allyl alcohol	$C_3H_6O I=$	58.0	"	0.8540	1.4135	28.08	25.74	16.95	15.29	19.87	17.46	"
Allyl acetate	$C_5H_8O_2 I=$	100.0	"	0.9276	1.4045	43.61	41.35	26.69	24.70	31.05	28.69	"
Allylacetic acid	$C_4H_6O_2 I=$	86.0	7.5°	0.9903	1.4341	43.83	41.38	26.30	24.70	30.56	28.14	Gladstone.
Methyl acrylate	$C_5H_8O_2 I=$	86.0	20.0°	0.9600	1.3984	35.69	33.67	21.64	20.69	25.52	22.85	Kahlbaum.
Methyl maleate	$C_6H_8O_4 I=$	144.0	"	1.1517	1.4415	55.20	52.98	33.08	30.96	38.29	36.25	Knopps.
Ethyl crotonate	$C_8H_{10}O_2 I=$	114.0	"	0.9108	1.4245	52.61	50.35	31.66	29.31	36.93	33.98	Brühl.
Acrolein	$C_3H_4O I=$	56.0	"	0.8410	1.3998	26.62	23.29	16.13	14.92	19.02	15.97	Gladstone.
Mesityl oxide	$C_9H_{10}O I=$	98.0	"	0.8578	1.4440	50.72	45.78	30.34	26.96	35.13	30.95	Brühl.
Furfural	$C_5H_4O_2 I=$	96.0	"	1.1504	1.5261	43.56	38.35	25.41	20.38	28.54	21.58	"
Heptidene	$C_7H_{12} I=$	112.0	"	0.7458	1.4207	54.15	50.76	32.61	30.11	38.12	33.75	"
Octylene	$C_8H_{16} I=$	112.0	"	0.7197	1.4132	64.30	61.44	38.82	36.88	45.49	42.12	"
Valerylene	$C_6H_{10} I=$	82.0	"	0.6786	1.4004	48.39	43.08	29.32	25.50	34.52	28.46	"
						Mean		Mean		Mean		
						2.53		2.53		1.82		
Benzene	$C_6H_6 I=$	78.0	10.0°	0.8903	1.5078	44.48	37.08	26.11	21.18	29.50	21.90	Gladstone.
"	$C_6H_6 I=$	"	20.0°	0.8799	1.5014	44.44	37.08	26.14	21.18	29.60	21.90	Brühl.
Toluene	$C_7H_8 I=$	92.0	7.5°	0.8704	1.4982	52.76	44.76	30.99	25.79	35.22	27.19	Gladstone.
"	$C_7H_8 I=$	"	20.0°	0.8656	1.4955	52.66	44.76	31.05	25.79	35.21	27.19	Brühl.
O-Xylene	$C_8H_{10} I=$	106.0	18.0°	0.8632	1.4966	60.98	52.44	35.90	30.40	40.75	32.48	Gladstone.
M-Xylene	$C_8H_{10} I=$	"	15.5°	0.8726	1.5020	60.98	52.44	35.85	30.40	40.60	32.48	"
P-Xylene	$C_8H_{10} I=$	"	16.0°	0.8488	1.4846	60.52	52.44	35.75	30.40	40.76	32.48	"
Ethylbenzene	$C_8H_{10} I=$	106.0	20.0°	0.8673	1.4959	60.61	52.44	35.74	30.40	40.76	32.48	Landolt.
Mesitylene	$C_9H_{12} I=$	120.0	"	0.8558	1.4912	68.87	60.12	37.42	35.01	46.19	37.77	Brühl.
Cumene	$C_9H_{12} I=$	"	12.0°	0.8432	1.4801	68.33	60.12	37.42	35.01	46.16	37.77	Gladstone.
Cymene	$C_{10}H_{14} I=$	134.0	22.6°	0.8530	1.4847	76.14	67.80	45.00	39.62	51.28	43.06	"
Naphthalene	$C_{10}H_8 I=$	128.0	98.4°	0.9021	1.5823	77.47	58.80	44.42	33.14	58.96	33.22	Nasini.
Dimethylnaphthalene	$C_{12}H_{12} I=$	156.0	16.4°	1.0180	1.6157	94.35	74.16	53.52	42.30	68.39	43.80	"
Phenol	$C_6H_6O I=$	94.0	21.0°	1.0598	1.5509	48.86	39.78	30.25	25.52	31.49	23.49	Gladstone.
Cresol	$C_7H_8O I=$	108.0	23.0°	1.0390	1.5419	56.32	47.46	32.46	27.13	36.53	28.78	"
M-Cresol	$C_8H_{10}O I=$	"	19.0°	1.0330	1.5364	56.08	47.46	32.63	27.13	36.50	28.78	"
α -Naphthol	$C_{10}H_8O I=$	144.0	98.7°	1.0934	1.6206	81.58	61.50	46.21	34.50	50.33	34.81	Nasini.
Methyl benzoate	$C_8H_8O_2 I=$	136.0	20.0°	1.0862	1.5169	64.72	55.39	37.86	32.05	42.66	34.17	Landolt.
Benzyl isobutyrate	$C_{11}H_{14}O_2 I=$	178.0	23.0°	1.0058	1.4910	86.88	78.43	51.21	45.58	58.03	50.04	Gladstone.
						Mean		Mean		Mean		
						2.88		2.88		1.81		

erally confirmed by the nitrites of table III," and that "the higher value is where nitrogen exists in organic bases and amides." In a list of values which he gives to prove 5.1 to be an approximate value for nitrogen are given those for aniline and xylidine which are 6.39 and 6.15, respectively, instead of 5.1. This discrepancy Gladstone explains as due to the great depression of aniline and xylidine.

Table XIV has been made with the above statements of Gladstone as a basis. It will be noticed that the numbers for the bases are in the majority of cases very close to those found for the nitrites. The general average of the values for nitrogen in the bases is higher than that for the nitrites, in part on account of some abnormally high values such as those for methyldiphenylamine.

If the two very high numbers for methyldiphenylamine be rejected in the case of the Gladstone formula, the average for the bases is 5.40 instead of 5.80, as shown in the table. It will be noticed that in the case of the other two formulæ the average numbers for the nitrites are higher in both cases than the average numbers for nitrogen in the bases. If the first division of table XIV be separated into groups showing the difference for nitrogen when the nitrogen belongs to one of the three groups —NH_2 , =NH , ≡N , where the horizontal lines represent the number of unions with carbon—a union such as that of pyridine being counted as three—we find the following averages for the nitrogen for the three formulæ in the usual order.

For the group —NH_2 :

	Formula	$\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N	4.46	2.39	2.28
“ “	4.40	2.31	2.08
“ “	3.74	2.05	1.77
“ “	3.98	2.16	1.83
“ “	6.12	2.89	2.08
“ “	6.48	2.99	2.11
“ “	5.91	2.64	1.74
Mean	5.01	2.49	1.99

TABLE XIV.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at $t/4^\circ$	Ind. refr.	$P(M-1)$			$P(M^2-1)$			$P(M-1)$			Data of
						Found.	Calc'd	Diff.	Found.	Calc'd	Diff.	Found.	Calc'd	Diff.	
Diethyl amine	$C_4H_{11}N$	73.0	19.0°	0.7092	1.3871	39.84	35.22	4.62	24.24	21.68	2.56	28.72	26.08	2.64	Gladstone.
Triethyl "	$C_6H_{15}N$	101.0	"	0.7317	1.4005	55.28	50.58	4.70	33.49	30.90	2.59	39.47	36.66	2.81	"
Propyl "	C_3H_9N	59.0	23.5°	0.7140	1.3973	32.00	27.54	4.46	19.46	17.07	2.39	23.07	20.79	2.28	"
"	"	"	6.5°	0.7329	1.3968	31.94	27.54	4.40	19.38	17.07	2.31	22.81	20.79	2.08	"
Dipropyl "	$C_6H_{15}N$	101.0	23.2°	0.7356	1.4025	55.27	50.58	4.69	33.46	30.90	2.56	39.42	36.66	2.76	"
"	C_3H_9N	143.0	22.8°	0.7535	1.4171	80.15	73.62	6.53	44.71	44.73	2.98	56.56	52.53	4.03	"
Tri propyl "	$C_9H_{21}N$	"	4°	0.7793	1.4248	78.86	73.62	5.24	47.45	44.73	2.72	55.19	52.53	2.66	"
Allyl "	C_3H_7N	57.0	19.0°	0.7684	1.4200	31.16	27.42	3.74	18.77	16.72	2.05	21.94	20.17	1.77	"
"	"	"	10.5°	0.7754	1.4272	31.40	27.42	3.98	18.88	16.72	2.16	22.00	20.17	1.83	"
Methyldiphenyl amine....	$C_{13}H_{13}N$	183.0	20.0°	1.0476	1.6193	108.17	97.62	10.55	61.31	56.75	4.56	66.80	63.41	3.39	Brühl.
"	"	"	24.6°	1.0466	1.6166	107.81	97.62	10.19	61.14	56.75	4.39	66.70	63.41	3.29	Gladstone.
Pyrraline	C_8H_7N	69.0	13.0°	0.9606	1.5074	36.45	32.10	4.35	21.39	19.17	2.22	24.17	22.18	1.99	"
Aniline	C_6H_7N	93.0	20.0°	0.9986	1.5728	61.38	47.22	6.48	35.29	32.30	2.99	39.02	36.91	2.11	Brühl.
Toluidine	C_8H_9N	107.0	20.0°	1.0867	1.5585	68.49	62.58	5.91	39.55	36.91	2.64	43.94	42.20	1.74	Gladstone.
Xylidine	$C_8H_{11}N$	121.0	19.0°	0.9575	1.5585	70.60	62.58	8.02	40.79	36.91	3.88	45.29	42.20	3.09	Brühl.
Dimethylaniline	$C_8H_{11}N$	"	20.0°	1.0619	1.6118	105.43	97.62	7.81	59.88	55.75	4.13	65.41	63.41	2.00	Gladstone.
Benzylaniline	$C_{12}H_{13}N$	183.0	24.8°	0.9792	1.5088	41.05	36.66	4.39	24.08	21.27	2.81	27.11	23.67	3.54	Berliuer.
Pyridine	C_5H_5N	79.0	20.0°	0.9469	1.5026	48.58	44.34	4.24	29.01	25.88	3.13	32.33	28.86	3.49	"
Picoline	C_7H_7N	93.0	23.5°	0.9469	1.5006	49.48	44.34	5.14	29.09	25.88	3.21	32.97	28.86	4.11	Gladstone.
Piperidine	$C_5H_{11}N$	85.0	20.0°	0.8622	1.4449	43.86	39.90	3.96	26.23	24.13	2.10	30.35	28.09	2.26	Berliuer.
Quinoline	C_9H_7N	129.0	"	1.0947	1.6171	72.72	67.02	5.70	41.23	38.66	2.57	44.96	42.87	2.09	"
"	"	"	"	1.1021	1.6330	74.10	67.02	7.08	41.80	38.66	3.14	45.37	42.87	2.50	Gladstone.
"	"	"	18.0°	1.0960	1.6282	73.94	67.02	6.92	41.78	38.66	3.12	45.41	42.87	2.54	"
Propionitrile	C_3H_5N	55.0	19.0°	0.7862	1.3681	25.75	21.54	5.80	15.76	12.75	2.92	18.92	14.23	2.63	Gladstone.
Valeronitrile	C_5H_7N	83.0	18.0°	0.8010	1.3917	40.59	36.92	3.67	24.65	21.97	2.68	29.16	24.81	4.35	"
Capronitrile	C_7H_9N	97.0	"	0.8040	1.4087	49.31	44.60	4.71	29.81	26.58	3.23	35.00	30.10	4.90	"
Benzonitrile	C_7H_5N	105.0	"	1.0052	1.5306	54.36	48.90	5.46	31.67	27.98	3.69	35.52	30.35	5.17	"
"	C_5H_5N	"	20.0°	1.0076	1.5289	54.06	48.90	5.16	31.52	27.98	3.54	35.36	30.35	5.01	Berliuer.
Trimethylene cyanide....	$C_3H_6N_2$	94.0	23.2°	0.9888	1.4365	41.49	32.40	4.56	24.87	18.73	3.57	28.88	19.89	4.60	"
"	"	"	"	"	"	Mean	Mean	4.63	"	"	3.20	"	"	4.79	"

For the group =NH :

	Formula	$\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N	4.62	2.56	2.64
"	" 4.69	2.56	2.76
"	" 4.35	2.22	1.99
"	" 7.81	4.13	2.00
"	" 3.96	2.10	2.26
Mean	5.09	2.71	2.35

For the group $\equiv N$:

	Formula	$\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N	4.70	2.59	2.81
"	" 6.53	2.98	4.03
"	" 5.24	2.72	2.66
"	" 10.55	4.56	3.39
"	" 10.19	4.39	3.29
"	" 8.02	3.88	3.09
"	" 4.39	2.81	3.54
"	" 4.24	3.13	3.49
"	" 5.14	3.21	4.11
"	" 5.70	2.57	2.09
"	" 7.08	3.14	2.50
"	" 6.92	3.12	2.54
Mean	6.56	3.26	3.13

If, in the second group, 7.81 be taken from the first column and 4.13 from the second, both averages would be smaller than found in group $-\text{NH}_2$ for the corresponding formulæ.

If, from the first column of the third group, the numbers 10.55, 10.19, and 8.02 be rejected, the average is still 5.54; therefore, all three formulæ show higher numbers for the group $\equiv N$ than for either of the other groups. We may sum up the result of the grouping as follows:

	Formula	$\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N in the group				
$-\text{NH}_2$	5.01	2.49	1.99
Difference for N in the group				
$=\text{NH}$	5.09	2.71	2.35
Difference for N in the group				
$\equiv N$	5.54	3.26	3.13
Difference for N in cyanides,	4.63		3.20	4.79

It will be noticed that there is a gradual increase in the numbers for the formula $\frac{P(M-1)}{MD}$ from group —NH_2 to group $\equiv\text{NH}$, which would indicate that the union with carbon gave greater numbers for nitrogen than that with hydrogen. The large differences for nitrogen accounted for, by Gladstone, by their great dispersion are easily accounted for in the formula $\frac{P(M-1)}{MD}$ by the number of unions with carbon. While the numbers for the first two groups are too close together to be of much practical value, the numbers for groups 3 and 4 are far enough from each other and from groups 1 and 2 to be of value in determining whether nitrogen has three unions with carbon or is nitrogen of a cyanide. This is not true of the other two formulæ.

Chlorine, Bromine, and Iodine.

Since the values found in this paper for CH_2 so nearly agree with the values found by others for CH_2 , when either the Gladstone or the Lorentz-Lorenz formula was used, it might be expected that the values for the halogens would not differ much from those found by others. Gladstone has found for his formula: 9.9 for chlorine; 15.3 for bromine; and 24.5 for iodine. Haagen, using the same formula, found 9.8 for chlorine; 15.3 for bromine; and 24.8 for iodine. For the same formula I find—withstanding the different values for carbon and hydrogen—10.11 for chlorine; 15.32 for bromine; and 25.09 for iodine. The numbers found by Haagen and Gladstone were for red hydrogen light while those found in this paper are for sodium light. Conrady, using numbers for sodium light found 5.998 for chlorine, 8.927 for bromine; and 14.12 for iodine, for the Lorentz-Lorenz formula, while in this paper I have found 6.03 for chlorine; 8.84 for bromine; and 14.01 for iodine. These numbers agree also very closely with those found by Brühl for red hydrogen light: 6.02 for chlorine; 8.95 for bromine; and 13.99 for iodine.

For the formula $\frac{P(M-1)}{MD}$ the numbers found in this paper are 7.20 for chlorine; 9.95 for bromine; and 15.32 for iodine.¹

¹ See tables XV, XVI, and XVII for the method of determining these numbers.

TABLE XV.—Chlorine Derivatives.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at t°/4°	Ind. refr. Na light.	$\frac{P(M-1)}{D}$			$\frac{P(M^2-1)}{(M^2+2)D}$			$\frac{P(M-1)}{M/D}$			Data of
						Found	Calc'd - Cl.	Diff. for Cl.	Found.	Calc'd - Cl.	Diff. for Cl.	Found.	Calc'd - Cl.	Diff. for Cl.	
Propyl chloride.....	C ₃ H ₇ Cl	78.5	20.0°	0.8898	1.3886	34.28	24.54	9.74	20.84	14.91	5.93	24.69	17.51	7.18	Brühl.
Isobutyl "	C ₄ H ₉ Cl	92.5	19.0°	0.8626	1.3979	42.67	32.22	10.45	25.87	19.52	6.35	30.52	22.80	7.72	Gladstone.
Amyl "	C ₅ H ₁₁ Cl	106.5	20.0°	0.8740	1.4102	49.98	39.90	10.08	30.17	24.13	6.04	35.44	28.09	7.35	Jahn.
Ethylene "	C ₂ H ₄ Cl ₂	99.0	"	1.2501	1.4444	35.19	15.36	9.92	21.05	9.22	5.92	24.36	10.58	6.89	Weegmann.
Ethylidene "	"	"	"	1.2750	1.4168	35.16	15.36	9.90	27.15	9.22	5.98	24.78	10.58	7.10	"
Allyl "	C ₃ H ₅ Cl	76.5	"	0.9379	1.4154	33.91	24.42	9.49	20.44	14.56	5.88	23.96	16.89	7.07	Brühl.
Butyl "	C ₄ H ₉ Cl	106.5	"	1.0277	1.4121	42.71	32.47	10.24	25.75	19.71	6.07	30.24	22.90	7.34	"
Acetyl "	C ₂ H ₃ ClO	78.5	"	1.1051	1.3898	27.69	17.11	10.58	16.83	10.49	6.34	19.92	12.32	7.60	"
Chloral "	C ₂ H ₅ Cl ₃	147.5	"	1.5121	1.4557	44.46	14.11	10.12	26.49	8.33	6.05	30.54	9.04	7.17	"
Chloroform.....	CHCl ₃	119.5	"	1.4898	1.4898	35.84	6.18	9.89	21.41	3.53	5.96	24.77	3.65	7.04	Haagen.
Ethyl dichloracetate.....	C ₄ H ₆ Cl ₂ O ₂	157.0	"	1.5286	1.4807	62.41	32.17	10.08	37.27	19.01	6.08	43.02	21.21	7.27	"
Ethyl trichloracetate.....	C ₄ H ₅ Cl ₃ O ₂	191.5	"	1.5321	1.4866	53.71	33.67	10.02	32.17	20.09	6.04	37.33	22.85	7.24	Brühl.
Monochlorobenzene.....	C ₆ H ₅ Cl	112.5	"	1.1066	1.5248	53.35	44.22	9.13	31.14	25.53	5.61	34.99	28.24	6.75	"
"	"	22.5°	"	1.1066	1.5248	53.35	44.22	9.13	31.14	25.53	5.61	34.99	28.24	6.75	"
Monochlorotoluene.....	C ₇ H ₇ Cl	126.5	19.0°	1.1047	1.5232	53.28	44.22	9.06	31.12	25.53	5.59	34.98	28.24	6.74	Gladstone.
Benzyl chloride.....	C ₇ H ₇ ClO	140.5	7.0°	1.0761	1.5271	61.96	51.90	10.06	36.14	30.14	6.00	40.57	33.53	7.04	"
Benzoyl chloride.....	C ₇ H ₅ ClO	140.5	7.0°	1.0990	1.5415	61.93	51.90	10.03	36.19	30.14	6.04	40.17	33.53	6.64	"
Tetrahydronaphthalene dichloride.....	C ₁₀ H ₈ Cl ₂	199.0	20.0°	1.2122	1.5837	64.18	52.15	12.03	37.12	30.33	6.79	41.31	33.63	7.68	Brühl.
		18.0°	"	1.2648	1.6247	98.29	76.08	11.10	35.60	44.00	5.80	64.49	49.18	7.65	Ketteler.
						Mean	10.11				6.03			7.20	

TABLE XVI.—Bromine Derivatives.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at $t^{\circ}/4^{\circ}$	Ind. refr. Na-light.	$\frac{P(M-1)}{D}$			$\frac{P(M^2-1)}{(M^2+2)D}$			$\frac{P(M-1)}{MD}$			Data of
						Found	Calc'd	Diff.	Found	Calc'd	Diff.	Found	Calc'd	Diff.	
Ethyl bromide.....	C_2H_5Br	109.0	20.0°	1.4555	1.4239	31.74	16.86	14.88	19.48	10.30	9.18	22.29	12.22	10.09	Weegmann.
"	"	"	"	1.4569	1.4241	31.73	16.86	14.87	19.10	10.30	8.80	22.28	12.22	10.08	Haagen.
Propyl "	C_3H_7Br	123.0	"	1.3520	1.4339	39.47	24.54	14.93	23.68	14.91	8.77	27.53	17.51	10.02	Brühl.
Isopropyl "	"	"	"	1.3097	1.4251	39.93	24.54	15.39	24.02	14.91	9.11	26.01	17.51	10.50	"
Amyl "	$C_5H_{11}Br$	151.0	"	1.2202	1.4412	55.42	39.99	15.32	33.17	24.13	9.04	38.45	28.09	10.36	Haagen.
Allyl "	C_3H_5Br	121.0	"	1.3980	1.4655	40.29	24.42	15.87	23.74	14.56	9.18	27.43	16.86	10.54	Brühl.
Acetylene dibromide.....	$C_2H_2Br_2$	186.0	"	2.2289	1.5437	45.37	15.24	15.07	26.32	8.87	8.73	29.39	9.96	9.72	Weegmann.
Acetylene tetrabromide...	$C_2H_2Br_4$	346.0	"	2.9673	1.6380	74.39	12.36	15.51	41.90	7.06	8.71	45.42	7.30	9.53	"
Ethylene bromide.....	$C_2H_4Br_2$	188.0	"	2.1768	1.5379	46.45	15.36	15.55	27.00	9.22	8.89	30.21	10.58	9.82	"
Ethylidene "	"	"	"	2.0555	1.5128	46.01	15.36	15.75	27.47	9.22	9.13	31.01	10.58	10.22	"
Amylene "	$C_5H_{10}Br_2$	230.0	21.0°	1.6560	1.5976	70.50	38.40	16.05	41.35	24.56	8.40	46.76	26.45	10.16	Gladstone.
Bromoform	$CHBr_3$	253.0	20.0°	2.8189	1.5890	52.85	6.18	15.56	30.23	3.53	8.90	33.26	3.65	9.87	Jahn.
Bromobenzene.....	C_6H_5Br	157.0	"	1.4914	1.5598	58.92	44.22	14.70	34.02	25.53	8.49	37.37	28.24	9.13	Brühl.
"	"	"	23.5°	1.4925	1.5577	58.66	44.22	14.44	33.88	25.52	8.35	37.65	28.24	9.41	Gladstone.
Bromtoluene.....	C_7H_7Br	171.0	25.2°	1.4192	1.5608	67.56	51.00	15.66	39.01	30.14	8.87	43.29	33.53	9.76	"
α -Bromnaphthalene	$C_{10}H_7Br$	207.0	16.5°	1.4847	1.6565	91.54	74.58	16.96	51.25	42.92	8.33	55.26	47.54	7.72	Kanonnikoff.
"	"	"	"	1.4888	1.6601	91.78	74.58	17.20	51.32	42.92	8.40	55.23	47.54	7.69	Nasini.
β -Bromnaphthalene.....	"	"	"	1.5678	1.6669	88.06	74.58	13.48	49.12	42.92	6.20	52.83	47.54	5.29	Gladstone.
"	"	"	18.0°	1.5403	1.6630	89.09	74.58	14.51	49.78	42.92	6.86	54.17	47.54	6.63	"
Mean with the bromnaphthalene rejected								15.32			8.84			9.95	

TABLE XVII.—Iodine Derivatives.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at $t^{\circ}/4^{\circ}$	Ind. of refl. for Na-light.	$\frac{P(M-1)}{D}$			$\frac{P(M^2-1)}{(M^2+2)D}$			$\frac{P(M-1)}{MD}$		Data of
						Found.	Calc'd.	Diff. for I.	Found.	Calc'd.	Diff. for I.	Found.	Calc'd.	
Methyl iodide.....	CH_3I	142.0	20.0°	2.2532	1.5297	33.30	9.18	24.12	19.41	5.69	13.72	21.77	6.93	14.84 Haagen.
" "	"	"	21.0°	2.2740	1.5293	33.04	9.18	23.86	19.26	5.69	13.57	21.61	6.93	14.68 Gladstone.
Ethyl "	$\text{C}_2\text{H}_5\text{I}$	156.0	20.0°	1.9395	1.5731	41.46	16.36	24.60	24.30	10.30	14.00	27.40	12.22	15.18 Haagen.
Propyl "	$\text{C}_3\text{H}_7\text{I}$	170.0	"	1.7427	1.5951	49.16	24.54	24.62	28.93	14.91	14.02	32.66	17.51	15.15 Brühl.
Isopropyl "	"	"	"	1.7033	1.4997	49.86	24.54	25.32	29.34	14.91	14.43	33.25	17.51	15.74 " "
Butyl "	$\text{C}_4\text{H}_9\text{I}$	184.0	"	"	1.5091	56.91	32.22	24.69	33.47	19.52	13.95	37.94	22.80	15.14 " "
Isobutyl "	"	"	"	1.6056	1.4960	56.78	32.22	24.56	33.47	19.52	13.95	37.99	22.80	15.19 " "
Isobutyl "	"	198.0	14.0°	1.5048	1.4960	65.26	39.90	25.36	38.43	24.13	14.30	43.62	28.09	15.53 Gladstone.
Isoamyl "	$\text{C}_5\text{H}_{11}\text{I}$	"	20.0°	1.4703	1.4998	66.09	39.90	26.19	38.93	24.13	14.80	45.00	28.09	16.91 Haagen.
Sec-amyl "	"	"	"	1.4193	1.4948	73.90	47.88	26.32	43.52	28.74	14.78	49.44	33.38	16.06 Gladstone.
Sec-hexyl "	$\text{C}_6\text{H}_{13}\text{I}$	212.0	19.0°	3.3188	1.7421	59.95	7.68	26.14	32.64	4.61	14.02	34.41	5.29	14.56 " "
Methylene diiodide.....	CH_2I_2	268.0	"	2.5890	1.6479	74.06	23.04	25.52	41.59	13.71	13.94	44.94	15.87	14.54 " "
Trimethylene iodide	$\text{C}_3\text{H}_6\text{I}_2$	296.0	7.5°	"	"	"	"	"	"	"	"	"	"	"
Iodobenzene	$\text{C}_6\text{H}_5\text{I}$ $\text{I}=\text{C}_3$	192.0	22.2°	1.8300	1.6197	69.07	44.22	24.85	39.13	25.53	13.60	42.65	28.34	14.31 " "
						Mean	25.09				14.01			15.22

Sulphur.

Divalent sulphur, like oxygen, has two very different values for its atomic refraction: one when its union corresponds to hydroxyl- or ether-oxygen, and another when its union corresponds to carbonyl oxygen. As in the case of oxygen the second value is the higher and enough higher to be of value in determining the kind of union with carbon. This would indicate that the kind of union is much the same for sulphur and oxygen whatever the union may be. Table XVIII will show these different values and the method of obtaining them.

Carbon disulphide has been calculated as having one carbonyl sulphur and one ether-sulphur. Ethyl sulphocarbonate and ethyl dithiosulphocarbonate illustrate the influence of the dispersive power of sulphur on the numbers obtained for sulphur. For the Gladstone and Lorentz-Lorenz formulæ, the first gives a number about as much below as the second does above the mean. The mean corresponds to the numbers obtained from the substances having two atoms of sulphur in the molecule. The formula $\frac{P(M-1)}{MD}$ would indicate that carbon disulphide is not truly represented by a carbonyl sulphur atom and an ether-sulphur atom.

E. Wiedemann,¹ found that for the Gladstone formula the numbers for sulphur were greater the greater the proportion of sulphur in the substance. He also found for the Lorentz-Lorenz formula two values for sulphur: 7.93 for sulphur of sulphides and hydrosulphides (hydroxyl or ether-unions), and 9.29 for carbonyl unions.

In conclusion I give the following comparative table. The numbers in column I are those given by Gladstone² for ray A, and are the same as those given by Landolt and others for ray H α (C). In column II are given Landolt's numbers³ for ray A. The numbers found in this paper for ray H α are given in column III, and for ray N α (D) are given in column IV. Column V contains Landolt's numbers³ for ray A. Brühl's

¹ Ann. der phys. Wied., **17**, 577, (1882).

² J. Chem. Soc., **45**, 244, (1884).

³ Ann. Chem. (Liebig), **213**, 112 (1882).

numbers¹ for ray Ha(C) are given in column VI. Column VII contains Conrady's numbers.² Columns VIII, IX, X, and XI contain numbers found in this paper.

	$\frac{P(M-1)}{D}$			$\frac{P(M2-1)}{(M2+2)D}$					$\frac{P(M-1)}{MD}$		
	I. Ray A.	II. Ray A.	III. Ray Ha.	IV. Ray Na(D).	V. Ray A.	VI. Ray Ha(C).	VII. Ray Na(D).	VIII. Ray Na(D).	IX. Ray Ha(C).	X. Ray Ha(C).	XI. Ray Na(D).
Carbon, saturated.....	5.0	4.86	4.61	4.68	2.43	2.48	2.501	2.45	2.33	2.00	2.01
" in Cn Hn	5.95
" double linked	6.1	5.86
" standing alone.....	4.68(?)	2.45(?)	2.01(?)
" double linking increment i=	2.00	...	2.88	1.59	1.78	1.707	1.81	2.66
Hydrogen.....	1.3	1.29	1.50	1.50	1.02	1.04	1.051	1.08	1.11	1.64	1.64
Oxygen hydroxyl	2.80	2.71	2.72	2.70	1.56	1.58	1.521	1.46	1.52	1.63	1.59
" ether	2.70(?)	1.683	1.46(?)	2.13
" carbonyl.....	3.40	3.29	2.27	3.25	2.29	2.34	2.287	2.35	2.37	3.30	3.38
Nitrogen in -NH ₂	5.01	2.49	1.99
" " =NH ₁	5.10	5.09	...	3.02(?)	...	2.71(?)	2.35
" " \equiv N	5.54	3.26	3.13
" " cyanides.....	4.10	4.63	3.20	4.79
Chlorine	9.9	9.53	...	10.11	5.89	6.02	5.998	6.03	7.20
Bromine	15.3	14.75	...	15.32	...	8.95	8.927	8.84	9.95
Iodine	24.5	23.55	...	25.09	...	13.99	14.12	14.01	15.22
Sulphur in place of hydroxyl oxygen.....	14.1	13.47	7.66	8.36
" " carbonyl	16.0	14.74	...	19.76	11.02	11.85

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¹ Ztschr. phys. Chem., 1, 306 (1887).

² Ztschr. phys. Chem., 3, 226 (1889).

A NEW APPARATUS FOR DETERMINING MOLECULAR WEIGHTS BY THE BOILING-POINT METHOD.

BY H. B. HITE.

In determining molecular weights by the boiling-point method, one of the principal sources of error is that due to changes in atmospheric pressure, errors from this source alone being quite sufficient, often, to render the results absolutely worthless. Indeed, one who has not had occasion to make accurate readings of the barometer *at short intervals* would hardly believe how great or how capricious these changes may be. The correction for such errors may be obtained from the barometer directly, or better, from a second boiling-point apparatus, but there is no apparatus that of itself makes any attempt to correct for these errors.

Two years ago, work was begun in this laboratory on an apparatus which, it was hoped, would not only be entirely independent of changes in atmospheric pressure, but tend to eliminate a number of other errors. The method was briefly as follows :

Instead of using one boiling-flask and a thermometer, it was proposed to use two flasks, each carrying in the position usually occupied by the thermometer, a tube containing one set of the terminals of a thermopile. Any difference in the temperature of the two boiling liquids, such as would be caused by the dissolution of some substance in one of them could be measured with a galvanometer ; or the molecular weight of the substance could be determined from the amount of known substance that would have to be added to the other flask to bring the galvanometer to its original position. Changes in atmospheric pressure, however, would not be recorded as they would affect both liquids alike. Many advantages of such a method will suggest themselves. But there were also some disadvantages connected with it, and some of these became more apparent as the work proceeded. The Beckmann apparatus was found to be poorly adapted to such work. It is fragile, complicated, and will vary with the heat applied to it. There are other causes of variation that

are not always so easy to discover. The movements of the thermometer in response to changes in atmospheric pressure are sluggish and uncertain; indeed, the general behavior of the apparatus is not always such as would be calculated to inspire the greatest confidence in it.

In the attempt to devise a simpler and more reliable boiling-apparatus—which required a great deal more time than had been anticipated,—the galvanometer method was lost sight of. It will, however, be taken up again in the near future, a number of improvements having meanwhile suggested themselves. But as the boiling-apparatus devised for this purpose can be used to advantage in determining molecular weights with a thermometer in the usual way, it is thought well to describe it before going further.

More than a hundred forms of apparatus were carefully fitted up and thoroughly tested. A number of these would determine molecular weights with considerable accuracy. Most of them would distinguish between multiples. It will be impossible in this connection to do more than mention a few of the typical forms.

Boiling by Means of an Electric Current.—One of the first forms tried was constructed as follows:

A large test-tube which served as a boiling vessel was closed by a stopper carrying the thermometer, condenser, and a small glass tube. This tube extended to near the bottom of the test-tube, and contained two insulated copper wires, the lower ends of which were connected by a loop of platinum wire. This extended beyond the end of the tube, which was closed upon the loop in the same way that the film is arranged in an incandescent lamp. The loop was then bent at right angles to the tube so that it would lie on, or near the bottom of the test-tube. The test-tube was suspended in an air-bath which furnished the heat to boil the liquid, while the hot wire caused the liquid in contact with it to burst into bubbles at once, and these prevented the liquid from becoming superheated. The boiling was very regular, the liquid appearing like a mass of bubbles. But, if the current was increased or decreased, the thermometer would fall or rise according as the temperature of the air-bath was much above or below the

boiling-point of the liquid. This apparatus was varied in many ways, but was never quite satisfactory.

Stirring the Liquid.—The freezing-point method has a decided advantage in that the ice remains in the liquid, and by stirring may be brought in contact with every part of it; while the bubbles which play an exactly similar part in a boiling liquid pass quickly to the surface. Then, the bubbles are not distributed uniformly, but start from a few points on the bottom of the glass. There will be upward currents over these points, and the bubbles passing to the surface *with* the current come in contact with still less of the liquid.

Again, heat must be added to the boiling liquid much more rapidly than it need be withdrawn from the freezing liquid. If, in the freezing-point method, it were necessary to under-cool the liquid until ice formed of its own accord, and, if the ice immediately escaped from the liquid to be melted and returned at a much higher temperature, it would be a far more difficult matter to get a constant freezing-point. If, on the other hand, in the boiling-point method, the liquid could be carefully super-heated a certain amount, a bubble dropped in to start the formation of bubbles, and if these could be stirred with the liquid until they had come in contact again and again, with every part of it, a constant boiling-point could be much more easily obtained. Hoping to approach these conditions, an apparatus was constructed as follows: A glass jar of $1\frac{1}{2}$ liters capacity, containing a liter of liquid was closed by a stopper carrying a thermometer and return-flow condenser, and placed in a double-walled air-bath, between the walls of which a liquid was kept boiling at a temperature above the boiling-point of the liquid in the jar. By means of a stirrer, the handle of which passed out through the condenser, it was an easy matter, not only to stir the liquid, but to keep it filled with bubbles. This is a very imperfect description of an apparatus that was fitted up with a great deal of care. The liquid was allowed to become super-heated about $1/2$ degree, and the stirring begun. The thermometer would fall, but it would continue to fall without so much as pausing at the boiling-point. The apparatus has since been greatly improved, and it is still hoped it may be made to give satisfactory results.

Thermometer in the Vapor.—The liquid in a distilling-bulb may be far from pure and yet the thermometer in the neck of the bulb will give the boiling-point of the pure liquid. The volume of vapor filling the flask is in contact with the solution only on one side, and that is far removed from the thermometer, while it is in contact on all other sides with the pure (distilled) liquid, wetting the walls, and this is at the boiling-point. If the vapor in contact with the thermometer bulb were surrounded by the solution instead of the distilled liquid it ought to give the boiling-point of the solution. In the hope of realizing these conditions, an apparatus was constructed as follows:

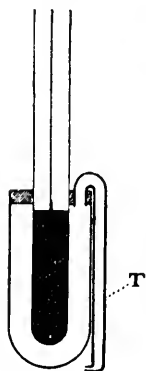


FIGURE 1.

follows: A Schleicher and Schüll filter-thimble (Fig. 1) was closed with a piece of cork which had a hole in the middle to admit the thermometer bulb. A small piece of glass tubing T bent as shown, passed through another hole in the cork. The thermometer bulb enclosed in the thimble in this way, was submerged in the liquid. When first submerged, the bulb is surrounded by air, but this is soon displaced by the rapid evaporation from the free, wet, inner walls of the thimble. When the liquid is boiling, the vapor pours out of the tube, T, which is slightly drawn out to a point and bent to one side so that the bubbles will escape more regularly. It is to be observed that in this arrangement the thermometer bulb is in the midst of a mass of vapor, which is in contact, practically, on all sides with the boiling solution. On heating the pure liquid to boiling, the thermometer rises steadily and remains perfectly constant or follows the barometer. On adding some substance to the liquid, the thermometer rises rapidly, at first, then more and more slowly, and does not reach the correct elevation in an hour, though continually approaching it. This apparatus, like all the other simple forms mentioned, was varied in many ways, but it was never satisfactory. As an apparatus for determining the absolute boiling-point of pure liquids, it might have some advantages, as the thermometer bulb is so well protected. The trouble in the case of solutions is probably due to the condensation on the thermometer bulb.

Balls of Platinum Gauze.—It is necessary that some part of

a liquid boiling under ordinary conditions should be heated considerably above its boiling-point, in order that bubbles may be formed. This, of course causes great irregularities in temperature. If there were always a liberal supply of bubbles remaining in the liquid, a much gentler heat would be sufficient. An apparatus constructed as follows was an attempt in this direction: A boiling-tube provided with a thermometer and condenser, arranged as usual, was placed in an air-bath, and filled to the surface of the liquid with hollow balls, 3 mm. in diameter, made of closely-woven platinum gauze. When the balls are dropped into the liquid, each encloses a bubble of air. This expands as the liquid is heated, until the pressure is sufficient to cause a part of the air to force its way out between the meshes of the gauze. The air is soon displaced by vapor. In this apparatus the boiling was very regular, and it could be used for determining molecular weights, but it is far less accurate than another apparatus that had meanwhile been devised, and for which work on all other forms was suspended, possibly before the apparatus just described had received the attention it deserved.

An Inverted Specimen Tube.—A boiling liquid is always super-heated, and the extent to which it is super-heated depends upon many circumstances, among which may be mentioned the character of the surface of the flask. A small rough place will serve as a starting-point for a stream of bubbles which will of course lower the temperature in that part of the flask. But specks and rough places in the glass can never be depended upon. They are liable to become inactive at any time. To promote regular boiling, Beckmann introduced what has been the characteristic feature of his apparatus ever since,—a platinum wire sealed in the bottom of the flask. Gernhardt states¹ that the bubbles do not start from the wire, but from the fusible glass used in fixing the wire. It is probable that the bubbles start from some small cracks or crevices around the wire or between the fusible glass and the flask. Instead of the platinum wire or the fusible glass, or both, the author would suggest the use of a small specimen tube, placed in the boiling tube, so that the open end rests on the bottom, and the closed end against the side of the boiling-tube. The lower

¹ Ber. d. chem. Ges., 27, 964.

part of the boiling-tube should be filled with beads as usual. There will always be a bubble at the end of the specimen-tube where the heat is being applied.

Boiling by Means of the Vapor.—Since a salt-solution may be heated far above the boiling-point of the pure solvent by passing its vapor through it, it seemed not improbable that, if the solution were carefully jacketed, and the vapor came directly from a salt-solution of the same concentration, an accurate boiling-point might be obtained in this way. At all events, it seemed highly improbable that the solution would be super-heated, and, as it was suspected that most of the difficulties with other forms of apparatus were due to super-heating the liquid, it was determined to give this idea a thorough trial. The first attempt was entirely satisfactory. The thermometer following the barometer for two days and the greater part of a night almost as closely as the two instruments could be read. Fig.

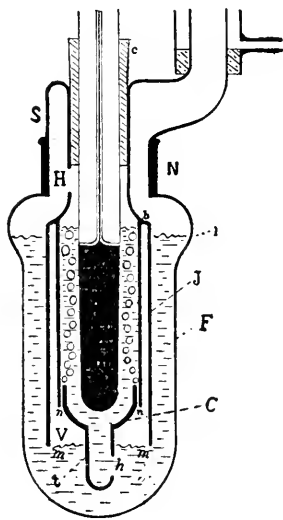


FIGURE 2.

2 shows one of the first forms used. It is a vertical section through the boiling flask and adjoining parts reduced one-half. A boiling-flask, *F*, is closed by a stopper *S*, which is ground into the neck *N*. This stopper opens into the condenser *K*, and the tube *T* is suspended from it. The lower, wider part of this tube, is jacketed by the tube *J*. The tubes are blown together as shown at *b*. The lower end of the tube *T* is closed by a cup-shaped stopper *C*, the bottom of which is drawn out into a short tube *t*, which has a hole, *h*, in the side, through which the liquid in the flask may mix with that in the tube *T*. The stopper *C*

has three or four small notches *n-n*, cut vertically across its ground surface with the sharp corner of a wet file. When the stopper is in position, these notches form so many small holes through which the vapor collected in the lower part of the jacket,—the space *V*,—may stream up into the liquid in the tube *T*. A hole *H*, allows it to pass out to the stopper *S*, and

into the condenser with the vapor from the flask. The condensed vapor is all returned to the flask. A thin cork stopper *c*, holds the thermometer in place. The flask is filled with liquid to the line *l-l*, and when boiling the vapor displaces the liquid from the jacket so that there is a free surface as indicated by the line *m-m*. The bottom of the flask is filled with balls of platinum-gauze, to within 2 or 3 mm. of the lower end of the jacket J. Beads may be used, but the balls are much better, and they are more easily cleaned and dried.

It is to be observed that the tube T, containing the liquid in contact with the thermometer bulb, is well protected, being almost entirely surrounded by the vapor which, in turn, is surrounded by a solution of exactly the same concentration, and, consequently, boiling at the same temperature as the solution in the tube. The liquid boiling in the flask is of course super-heated, but the vapor passing up through the notches can hardly super-heat the liquid in the tube T, as the super-heating would have to take place at the surface of the bubbles where evaporation can also take place.

On heating the liquid to boiling, the thermometer rises very slowly until the liquid in the flask begins to boil, and bubbles begin to pass through the notches in the stopper C, when it rises very quickly, and is constant in ten or twelve minutes. Not only does the thermometer quickly become constant, but it remains constant, even if the heat applied to the flask is varied much more than it ever need be during a determination. The heat may be increased three or fourfold, until the boiling is changed from gentle to almost violent, but the thermometer remains almost stationary. The apparatus has been put to this test again and again; the greatest elevation being 0.004° .

Few changes have been found necessary or advisable in this apparatus, although it has been in use in this laboratory for two years. The jacket J, was considered unnecessary, at least for all ordinary work and has been discarded. This made the small tube *t*, attached to the stopper C, unnecessary, as the liquid in the flask and tube T, could communicate at once through small holes *h-h* (Fig. 3). The tube T, is extended below the stopper C, to collect bubbles rising from the bottom of the flask.

The apparatus as now manufactured¹ is shown in Fig. 4.

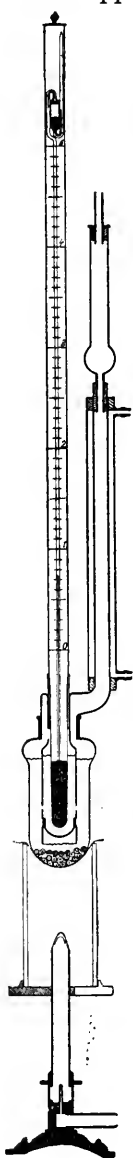


FIGURE 4.

The flask rests upon a piece of wire gauze, which rests upon a piece of glass tubing, which serves as a jacket for the Bunsen burner. A very small flame, with the air entirely turned off, is sufficient. The solvent is weighed out in the boiling-flask, which is detached from the condenser at the ground-joint J, (Fig. 3), and enclosed by another stopper ground to fit it. The substance is introduced through the condenser.

The vital part of the apparatus is the cup-shaped stopper C. This stopper should be carefully ground into place. The ground surface should be 4 or 5 mm. deep. The upper edge of the stopper should be 20 mm. above the lower end of the tube T, in order to secure a steady flow of bubbles through the notches, which should be deep enough for the vapor to pass through them freely, but not so deep that they will exhaust the vapor in the space V, faster than it can be collected. Three notches are sufficient.

The apparatus will not work with water, as the bubbles cannot force their way through the notches. It does not work with some heavy, high-boiling liquids, probably on account of the great difference in the temperature of the flask and the surrounding air. There are one or two liquids that

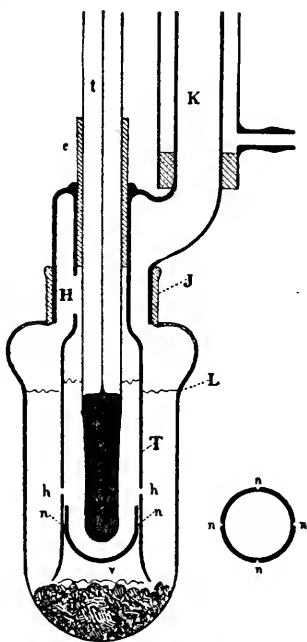


FIGURE 3.

¹ By Messrs. Eimer and Amend, New York.

do not work so well if beads are used, but if little balls of platinum gauze are used there is no low-boiling organic liquid so far as the author knows that does not work well.

The following determinations were made by students in this laboratory :

SOLVENT, ALCOHOL : MOLECULAR ELEVATION, 11.5.

Benzoic Acid, 122.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
49.110	0.5335	1.09	0.102	122.4	0.3
"	1.0912	2.22	0.195	122.5	0.4
"	1.3397	2.73	0.256	122.5	0.4
48.720	0.6210	1.28	0.120	121.9	0.1
"	0.8510	1.75	0.165	121.8	0.2
49.958	3.0535	6.11	0.573	122.7	0.6
"	3.4630	6.93	0.647	123.0	0.8
"	3.7785	7.56	0.704	123.0	0.8
"	4.0940	8.19	0.764	123.0	0.8
"	4.4850	8.97	0.842	122.6	0.5
"	4.8730	9.95	0.929	123.2	1.0
"	5.3525	10.71	0.994	123.9	1.5
"	5.8415	11.69	1.081	124.4	2.0
"	6.3405	12.68	1.172	124.5	2.0
"	6.7670	13.54	1.247	124.9	2.4

Urea, 60.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
34.223	0.3488	1.02	0.185	63.4	5.7
"	0.6724	1.97	0.355	63.6	6.0
"	0.8581	2.51	0.453	63.7	6.2
34.730	0.3233	0.93	0.170	63.0	5.0
34.156	0.3550	1.04	0.188	63.6	6.0
"	0.6945	2.03	0.366	63.9	6.5
"	0.9937	2.91	0.520	64.3	7.2

Acetamide, 59.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
31.159	0.2630	0.71	0.165	58.8	0.3
"	0.4500	1.44	0.277	60.0	1.7
31.037	0.2467	0.79	0.153	59.8	1.4
"	0.4711	1.52	0.289	60.4	2.4
"	0.8315	2.70	0.506	60.9	3.2
31.258	0.4171	1.33	0.254	60.4	2.4
"	0.9540	3.05	0.588	60.8	3.1

Acetanilide, 135.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
31.854	0.7058	2.21	0.189	134.9	0.1
"	1.0880	3.41	0.289	136.0	0.8
31.580	0.8295	2.62	0.223	135.4	0.3

Benzoic Acid, 122.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
47.560	0.4310	0.91	0.085	122.6	0.5
"	0.7152	1.50	0.142	121.8	0.2
"	1.0838	2.28	0.214	122.4	0.2
"	1.3965	2.94	0.276	122.3	0.2
"	1.6232	3.41	0.320	122.6	0.5
"	1.8987	3.99	0.376	122.1	0.1
"	2.1420	4.50	0.422	122.7	0.6
"	2.3848	5.02	0.469	123.0	0.8
"	2.6416	5.55	0.519	123.6	1.3
"	2.9790	6.27	0.579	124.4	2.0

Camphor, 152.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
33.667	1.0561	3.14	0.226	160.0	5.0
32.756	1.1371	3.47	0.249	160.0	5.0
55.510	0.1910	0.34	0.026	152.0	0.0
"	0.3272	0.59	0.045	151.0	1.0
"	0.5052	0.91	0.068	154.0	1.0
"	0.9017	1.62	0.120	156.0	3.0
"	1.2644	2.28	0.164	160.0	5.0
"	1.7994	2.34	0.230	162.0	7.0
"	2.2500	4.06	0.286	163.0	7.0
"	2.7142	4.89	0.340	166.0	9.0

SOLVENT, ETHER: MOLECULAR ELEVATION, 21.1.

Camphor, 152.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
29.540	0.7480	2.53	0.348	152.7	0.5
"	0.9666	3.28	0.450	153.4	0.9
"	1.2476	4.22	0.580	153.6	1.1
"	1.5268	5.17	0.706	154.3	1.5
"	1.8954	6.42	0.876	154.6	1.7

Iodine, I_2 , 253.1.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
31.048	2.0970	6.75	0.560	254.5	0.6
31.678	0.9152	2.89	0.241	252.9	0.1
"	1.5252	4.81	0.400	254.0	0.4

Naphthalene, 128.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
33.093	0.2830	0.86	0.140	128.9	0.7
"	0.5323	1.61	0.263	129.0	0.8
"	0.7683	2.32	0.379	129.3	1.0
"	0.8884	2.67	0.437	129.6	1.2
"	1.1036	3.35	0.542	129.9	1.5
"	1.3141	3.97	0.643	130.3	1.8
"	1.5288	4.62	0.745	138.8	2.2

SOLVENT, BENZENE: MOLECULAR ELEVATION, 26.7.

 $(P\text{NCl}_2)x.^1$

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation from 464.
37.618	1.1620	3.09	0.177	466.0	0.4
"	1.4820	3.94	0.227	463.0	0.2
37.987	1.1107	3.92	0.167	467.0	0.7

In conclusion, the author wishes to express his thanks to Professor Remsen, under whose immediate supervision the work above described was carried on.

CHEMICAL LABORATORY, JOHNS HOPKINS
UNIVERSITY, February, 1895.

Contributions from the Chemical Laboratory of Cornell University.

A NEW APPARATUS FOR THE DETERMINATION OF MOLECULAR WEIGHTS BY THE BOIL- ING-POINT METHOD.

W. R. ORNDORFF AND F. K. CAMERON.

Since Beckmann first proposed the apparatus, now so well known by his name, for the estimation of molecular weights from the elevation of the boiling-points of solutions, many modifications have been suggested, and recently, Beckmann²

¹ Determined for Dr. H. N. Stokes. See This Journal, 17, 288.

² Ztschr. phys. Chem., 15, 656.

himself has reviewed those descriptions of which have from time to time appeared in the literature.

The advantages of the boiling-point over the freezing-point method are many. In the first place, *any* solvent may be used and the precautions necessary to secure good results are far less numerous.¹ The solubility of substances is much greater at the boiling-point of the solvents than at their freezing-points, and there is no chance for the introduction of errors from some of the dissolved substance crystallizing out, as is the case with the freezing-point method. Notwithstanding these and other advantages of the boiling-point method, it has not been much used owing to the fact that with the apparatus hitherto proposed the time necessary for the determinations has been very great, so that, unless one selects a day when the barometer is practically constant, errors due to barometric changes cannot be avoided. A quick method of determining boiling-points would, of course, eliminate these errors, and would have the additional advantage of saving much time. In the course of an investigation by us it was necessary to make some molecular-weight determinations by the boiling-point method, using solvents of relatively high boiling-points. It soon became evident that the forms of apparatus as yet suggested, were not suited to our purpose, principally, in that stoppers of cork or rubber were acted on to such a degree by the solvents, as to completely interfere with the determinations. Moreover, glass stoppers were precluded because the unequal expansion of the stopper and neck of the vessel, prevented a tight joint, allowing the boiling liquid to distil off in quite appreciable amounts. Stoppers of asbestos and of plaster of Paris (mixed with water-glass) were also tried, and found either to leak or to be acted upon by the solvent.

As a result of our efforts to overcome these and other difficulties, we succeeded in devising an apparatus which worked in such a satisfactory manner with both high and low-boiling liquids and is withal so simple in construction, and readily assembled, that we present here a description with some determinations which will, we believe, demonstrate its useful-

¹ See in this connection: Loomis Physical Review, **1**, 199; and Nernst and Abegg, Ztschr. phys. Chem., **15**, 681.

ness to others. There is no part, save perhaps the differential thermometer, but will be found in any well equipped chemical laboratory.

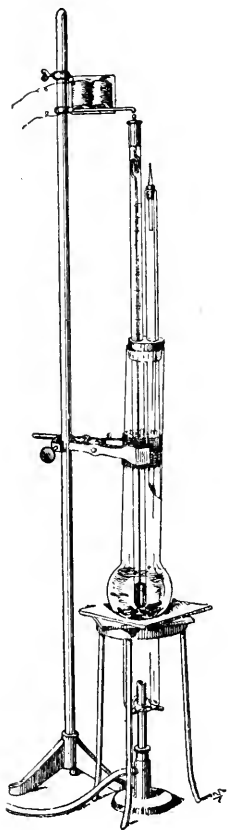
In detail, the apparatus of which a one-eighth scale drawing is given, consists of:

A bulbed flask, made by cutting off the mantle or outer jacket used in the Victor Meyer vapor-density method, to form a vessel about 30 cm. in length and 4 cm. in diameter. Preferably a tube with thin walls and narrow bulb should be selected.

A layer of some heavy material in the bottom of the vessel. This layer should be of some depth, a good conductor of heat, of as dense material as possible, and with roughened surfaces. Broken garnets, pellets of silver, etc., were tried by us, but the best results were obtained with pellets, made by rolling together, strips of scrap platinum, having the surfaces etched with *aqua regia*. Scrap platinum is to be found in every laboratory, is readily cleaned and prepared for a new determination by simple ignition, and works especially well because it is such a good conductor of heat, and has

such a high specific gravity. With a bulb of comparatively thin glass and from 30 to 40 grams of platinum pellets, very regular boiling can be obtained, fully as good as with the platinum wire fused into the bottom of the flask, and without the attendant weakening of the vessel.

A condenser, consisting of a straight tube about 13 mm. diameter, the lower end ground with a slant, so as to direct the returning solvent away from the thermometer. When properly adjusted, the lower end of this condenser tube will just touch the outer wall of the flask, returning the cooled solvent in such a way as to have a minimum effect upon the



thermometer readings. The upper end of this condenser was fitted with a stopper carrying a tube¹ with a capillary orifice. When very volatile liquids were used the condenser tube was lengthened, and the upper portion surrounded with a cold-water jacket in the usual manner. But in the case of higher boiling liquids (over 100° C.), it was usually sufficient to have it about the same height as the thermometer, with greatly increased convenience, since the material whose molecular weight was to be determined, was introduced through this tube.

The thermometer was a Beckmann differential instrument of the usual form, made by Göetze, of Leipzig. We found that the instruments furnished for boiling-point determinations are generally constructed with so fine a capillary tube that there is always more or less sticking of the mercury thread, and if the thermometer be struck sufficiently hard to prevent this, there is danger of the thread breaking, necessitating a resetting of the thermometer and a reweighing of the solvent. We therefore used thermometers made for freezing-point determinations, which have larger capillary tubes, precluding any sticking of the mercury, and what is very important, allowing the instrument to set rapidly. The large mercury bulbs of these instruments are undesirable for this work as they require a large amount of solvent and show a very appreciable aneroid barometer effect. These disadvantages are more than compensated for, however, by the increased sensitiveness of the instrument.² The thermometer and condenser tube are held in place by a rubber stopper fitted into the flask. In working with volatile liquids, which act upon rubber, an ordinary cork was substituted.

An outer mantle which surrounds the bulb of the flask, and reaches to about a centimeter above the surface of the boiling liquid. The mantle is not figured in the accompanying illustration. Wrappings of asbestos paper, asbestos cloth, and the non-conducting covers used on steam pipes³ were all tried

¹ When working with hygroscopic solvents this is replaced by a calcium chloride tube.

² Directions have been sent to Göetze for a differential thermometer, to be used for boiling-points, in which these difficulties will be obviated.

³ The non-conducting steam pipe covers made by Keasbey and Mattison, of Philadelphia, of porous magnesia and asbestos, were found to be particularly efficient.

with success. For convenience of manipulation, together with effectiveness, a scarf of asbestos cloth, which can be wrapped very closely around the bulb in four or five folds, is to be preferred.

A small electric hammer, operated by a current from a Daniell cell or gravity battery, was so mounted as to strike continuously the metal top of the thermometer.¹ By removing the gong from a small electric call-bell, a very good hammer for this purpose may be obtained. The thermometer was thus rendered extremely sensitive, making it necessary that the room should be free from draughts, and that the supply of heat should be approximately constant.

A source of heat, for which purpose was utilized a Bunsen burner of appropriate size, fitted with a glass chimney to protect the flame as much as possible from irregular draughts. As a rule an Elsler gas regulator for constant pressure, and a precision stop-cock were used. Experiments to determine their value indicated that they were not necessary. The size of the flame, which should be rather large than small, can be well regulated by using a Hofmann pinch-cock on the rubber tube connecting the burner with the gas supply. For very volatile liquids a small flame was obtained by drawing out a glass tube to proper size, and passing it through a cork fitted to the tube of the Bunsen burner.

The whole apparatus was clamped into position in the following way: A strip of fine copper gauze, about 4 cm. in width, was wrapped to several thicknesses, smoothly and tightly about the tube, and this was then firmly clamped (using naked metallic surfaces) to an iron stand. There was thus obtained a condenser, of large heat capacity and good radiating surface, to take the heat from the walls of the tube. This device was found to be quite efficient, and, in the case of the higher-boiling liquids, but very little of the solvent condensed above this guard. The bottom of the bulb rested upon a piece of fine copper gauze, slightly moulded to receive it, and this in turn was fitted over a circular orifice, of from 3 to 4 cm. in diameter, cut into heavy asbestos board.

The boiling of the liquid should be *quite rapid*, and to this

¹ Loomis (Physical Review, 1, 206) made use of a similar device in his freezing-point determinations, and calls attention to the necessity for its use.

end, as large a flame should be used as the conditions of the experiment will permit. We have found this to be a very important point for the successful use of this apparatus, and, after much time spent in experimenting, have shown that the best results are obtained when the liquid is boiled as rapidly as possible, without driving the solvent too far up the condenser tube. The excess of heat is thus removed by the condenser, and slight variations in the heat supply, due to increased or diminished gas pressure, or to air currents, have very little influence on the readings of the thermometer. The boiling of the solvent should be continued for about an hour, in order that the materials, of which the thermometer is constructed, may adjust themselves so that constant readings may be obtained. But this condition once reached, the determination may be made quickly and with precision, as the thermometer under the electric hammer is extremely sensitive and sets very rapidly. Usually, from two to three minutes after introducing some of the substance, very good readings could be obtained. Apparently, in some cases, the thermometer steadied and became constant more readily after the introduction of a small quantity of the material under examination, and this device was occasionally used.

The material of which the molecular weight is to be determined was introduced in the form of compressed tablets, made in the manner suggested by Beckmann. It is very desirable, whenever possible, that a liquid in which the material is readily soluble should be used. Much of the accuracy of the method depends upon the rapidity with which the thermometer sets, and the readings are taken, because errors due to changes in the barometric pressure are thus avoided. However, when from the nature of the case solvents of slight power must be used, we found it desirable to grind the solid material in an agate mortar, with alcohol (or some other readily volatile medium), to a thick paste, which was then moulded in the usual way and dried to constant weight in an air-bath. The tablets thus prepared are extremely fragile but can be handled with care, and usually crumble to a very fine powder on coming in contact with the boiling solvent, thus presenting a very large surface to its action.

That it is distinctly advantageous to make such determinations when the barometer is constant, or as nearly so as possible, goes without saying.

The readings were taken with a telescope provided with cross hairs and leveling adjustment, located about two meters from the thermometer scale. For ordinary work, however, readings made with a simple magnifying glass would be sufficiently accurate. The room was kept as free as possible from draughts, and to further eliminate this disturbing influence, the lower part of the apparatus was at times partially surrounded with a wooden box with good effect.

All the materials used in the determinations here recorded were very carefully purified before being used. The boiling-points of the solvents given are determinations made with a standardized thermometer which was entirely surrounded with the vapor of the boiling liquid.

When the latent heat of vaporization was known, it was used in calculating the molecular rise of the solvent, according to the well-known formula¹ of Van't Hoff-Arrhenius. In other cases we used the experimentally determined constant. The observations for the whole series of determinations were *always* taken before any of the results were calculated, so as to prevent, as far as possible, any prejudiced readings. The time required to make a series of determinations, after the thermometer had become constant, is given for each substance, though it is to be understood that this does not represent the shortest time in which it was possible to complete the series, for in many cases we purposely waited much longer than necessary to see if the readings of the thermometer would change. The average length of time for a series of six or eight determinations was about thirty minutes.

In the following tables we give the results obtained with this apparatus with low and high boiling liquids. The work in which carbon bisulphide, benzene, toluene, and naphthalene were used was done by Mr. G. L. Terrasse, an undergraduate student of this university, to whom we wish here to express our thanks.

The molecular weight and the molecular elevation of infi-

¹ Molecular rise = $\frac{0.0198 T^2}{H}$, T being the absolute boiling-point at 760 mm., and H the latent heat of vaporization.

nite dilution are given in each case, as well as the averages of the whole series of determinations. When the individual determinations do not differ very much from each other the averages are to be preferred, otherwise the molecular weight at infinite dilution is more reliable.

It is especially to be noted in connection with the following tables that the results are recorded exactly as they were observed. *No single determination has been omitted, nor has any series been eliminated.*

SOLVENT: CARBON DISULPHIDE.

Boiling-point, $46^{\circ}.0$ C. at 757.4 mm.

Molecular elevation for 100 grams, $23^{\circ}.75$.

Latent heat of vaporization 84.82 Cal. Regnault, 1862.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
128.47	0.5603	$0^{\circ}.082$	$24^{\circ}.1$	126
"	1.0495	$0^{\circ}.154$	$24^{\circ}.1$	127
"	1.5187	$0^{\circ}.222$	$24^{\circ}.0$	127
"	2.0388	$0^{\circ}.297$	$24^{\circ}.0$	127
"	2.5553	$0^{\circ}.370$	$23^{\circ}.8$	128
"	3.0343	$0^{\circ}.439$	$23^{\circ}.8$	128
"	3.5522	$0^{\circ}.517$	$24^{\circ}.0$	127
"	4.1600	$0^{\circ}.605$	$23^{\circ}.9$	127
At infinite dilution,			$24^{\circ}.0$	127
Average of determinations,			$24^{\circ}.0$	127

Time, 40 minutes.

Barometer, 749.2-749.3 mm.

SOLVENT: CHLOROFORM.

Boiling-point, $60^{\circ}.2$ at 741.7 mm.

Molecular elevation for 11 grams, $36^{\circ}.6$.

Latent heat of vaporization, 61.0 Cal. Regnault, 1862.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
204.00	0.6964	$0^{\circ}.100$	$37^{\circ}.4$	125
"	1.3532	$0^{\circ}.190$	$36^{\circ}.6$	128
"	2.0996	$0^{\circ}.298$	$37^{\circ}.0$	127
"	2.8397	$0^{\circ}.384$	$35^{\circ}.3$	133
"	3.4233	$0^{\circ}.452$	$34^{\circ}.3$	135
"	4.4750	$0^{\circ}.590$	$34^{\circ}.4$	136
At infinite dilution,			$37^{\circ}.5$	121
Average of determinations,			$35^{\circ}.9$	131

Time, 30 minutes.

Barometer, 758.6-758.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
204.01	0.7142	0°.096	35°.1	133
"	1.3671	0°.186	35°.6	132
"	2.0055	0°.275	35°.9	131
"	2.5902	0°.362	36°.5	128
"	3.4636	0°.480	36°.3	129
"	4.7272	0°.656	36°.3	129
At infinite dilution,			34°.7	134
Average of determination,			36°.0	130

Time, 30 minutes. Barometer, 756.7-756.6 mm.

SOLVENT: BENZENE.

Boiling-point, 79°.6 C. at 744.5 mm.

Molecular elevation for 100 grams, 26°.6.

Latent heat of vaporization, 93°.4 Cal. Schiff, 1886.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
91.986	0.2657	0°.053	23°.5	145
"	0.6388	0°.128	23°.6	144
"	1.0180	0°.205	23°.7	144
"	1.3995	0°.282	23°.7	144
"	1.8481	0°.378	24°.1	141
"	2.3384	0°.480	24°.2	141
"	2.9719	0°.612	24°.2	141
"	3.6349	0°.742	24°.0	142
At infinite dilution,			23°.6	144
Average of determinations,			23°.9	143

Time, 60 minutes. Barometer, 736.3-735.7 mm.

SOLVENT: TOLUENE.

Boiling-point, 109°.7 at 741.7 mm.

Molecular elevation for 100 grams, 35°.1.

Heat of vaporization, 83.55 Cal. Schiff.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
83.88	0.7318	0°.210	30°.8	145
"	1.4428	0°.405	30°.1	149
"	2.1202	0°.602	30°.5	147
"	3.1532	0°.897	30°.5	147
"	4.0997	1°.166	30°.5	147
"	5.0883	1°.448	30°.6	147
"	6.2043	1°.756	30°.4	148
"	7.3067	2°.061	30°.3	148
At infinite dilution,			30°.5	147
Average of determinations,			30°.5	147

Time, 45 minutes. Barometer, 736.4-736.2 mm.

SOLVENT: PYRIDINE.

Boiling-point, $114^{\circ}.2$ C. at 741.7 mm.Molecular weight for 100 grams, $26^{\circ}.9$.*Anthracene, 178.*

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
89.90	0.1467	$0^{\circ}.026$	$28^{\circ}.2$	170
"	0.2749	0 .049	$28^{\circ}.5$	168
"	0.6554	0 .110	$26^{\circ}.9$	178
At infinite dilution,			$27^{\circ}.9$	173
Average of determinations,			$27^{\circ}.8$	172
Time, 30 minutes.		Barometer, 749.9 mm. constant.		

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
87.22	0.6458	$0^{\circ}.074$	$24^{\circ}.4$	270
"	0.9432	0 .118	$26^{\circ}.6$	247
"	1.1507	0 .145	$26^{\circ}.8$	246
At infinite dilution,			$25^{\circ}.8$	252
Average of determinations,			$25^{\circ}.9$	254
Time, 30 minutes.		Barometer constant.		

SOLVENT: ETHYLENE BROMIDE.

Boiling-point, $128^{\circ}.8$ C. at 741.7 mm.Molecular elevation¹ for 100 gram, 63.2° .*Anthracene, 178.*

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
217.28	0.2142	$0^{\circ}.034$	$61^{\circ}.4$	182
"	0.3919	0 .063	$62^{\circ}.2$	181
"	0.6704	0 .110	$63^{\circ}.5$	177
"	1.1170	0 .184	$63^{\circ}.7$	176
At infinite dilution,			$63^{\circ}.2$	178
Average of determinations,			$62^{\circ}.7$	179
Time, 25 minutes.		Barometer, 749-748.5 mm.		

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
204.07	0.2659	$0^{\circ}.031$	$58^{\circ}.1$	265
"	0.5629	0 .073	$64^{\circ}.6$	239
"	0.8599	0 .106	$61^{\circ}.4$	251
"	1.1957	0 .161	$67^{\circ}.0$	230
"	1.5888	0 .215	$67^{\circ}.3$	229
At infinite dilution,			$62^{\circ}.7$	246
Average of determinations,			$63^{\circ}.7$	243
Time, 40 minutes.		Barometer, 744.0-743.9 mm.		

¹ This is the same constant that Beckmann obtained. Ztschr. phys. chem., 6, 462.

SOLVENT: ANISOL.

Boiling-point, $152^{\circ}.7$ at 741.7 mm.Molecular elevation for 100 grams, $44^{\circ}.3$.*Acetanilid*, 135.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
100.23	0.7783	$0^{\circ}.258$	$44^{\circ}.8$	133
"	1.4713	0.460	42.3	141
"	2.0654	0.631	41.3	145
At infinite dilution,			45.8	130
Average of determinations,			42.8	139

Time, 60 minutes. Barometer, 748.3 – 748.7 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
100.23	0.7482	$0^{\circ}.224$	$40^{\circ}.5$	147
"	1.2959	0.370	38.6	154
"	1.7435	0.490	38.0	157
"	2.2073	0.610	37.4	159
"	2.6673	0.720	36.5	163
"	3.0613	0.814	36.0	166
At infinite dilution,			43.7	137
Average of determinations,			37.8	157

Time, 60 minutes. Barometer, 747.2 – 747.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
99.84	0.5514	$0^{\circ}.165$	$40^{\circ}.3$	148
"	1.0747	0.310	38.9	153
"	1.5692	0.455	39.1	152
"	2.0467	0.565	37.2	160
"	2.4447	0.670	37.2	161
"	2.8532	0.760	35.9	166
At infinite dilution,			41.8	143
Average of determinations,			38.1	157

Time, 60 minutes. Barometer, 739.7 mm. constant.*Anthracene*, 178.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
104.96	0.5044	$0^{\circ}.110$	$41^{\circ}.1$	194
"	1.0140	0.215	40.0	199
"	1.4972	0.320	40.3	197
"	1.9666	0.415	39.8	200
"	2.4394	0.515	39.8	200
"	2.9144	0.703	45.5	175
At infinite dilution,			44.0	180
Average of determinations,			41.1	194

Time, 60 minutes. Barometer 738.3 – 737.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
94.73	0.6162	0°.172	47°.1	168
"	1.1898	0.290	41.9	188
"	1.7194	0.402	39.4	200
At infinite dilution,			43.4	182
Average of determinations,			42.8	185

Time, 25 minutes.

Barometer, 737.2-737.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
101.95	0.3800	0°.094	44°.9	176
"	0.7927	0.194	44.4	178
"	1.2089	0.285	44.8	184
At infinite dilution,			45.0	175
Average of determinations,			44.0	179

Time, 30 minutes.

Barometer constant.

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
100.27	1.0883	0°.200	44°.9	240
"	1.5397	0.280	44.5	243
"	2.0093	0.370	45.1	240
"	2.3917	0.430	44.0	246
"	2.7931	0.510	44.7	242
At infinite dilution,			44.3	244
Average of determinations,			44.6	242

Time, 55 minutes.

Barometer, 745.4-745.8 mm.

SOLVENT: PHENETOL.

Boiling-point, 167°.9 C. at 741.9 mm.

Molecular elevation for 100 grams, 49°.3.

Anthracene, 178.

Grams Solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
90.33	0.4788	0°.145	48°.7	180
"	0.7615	0.232	48.9	179
"	0.9930	0.310	50.2	175
"	1.2714	0.395	50.0	175
At infinite dilution,			48.5	182
Average of determinations,			49.5	177

Time, 50 minutes.

Barometer, 739.3-739.6 mm.

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
82.92	0.3182	0°.081	51°.5	233
"	0.5751	0.139	48.9	245
"	0.8812	0.208	47.8	251
"	1.1889	0.288	49.0	245
"	1.4239	0.343	48.8	246
"	1.7367	0.415	48.3	248
"	1.9996	0.474	48.0	250
"	2.2680	0.540	48.2	249
At infinite dilution,			49.2	244
Average of determinations,			49.2	246

Time, 45 minutes. Barometer, 743.2 mm. constant.

SOLVENT: NAPHTHALENE.

Boiling-point, 216°.7 C. at 741.9 mm.

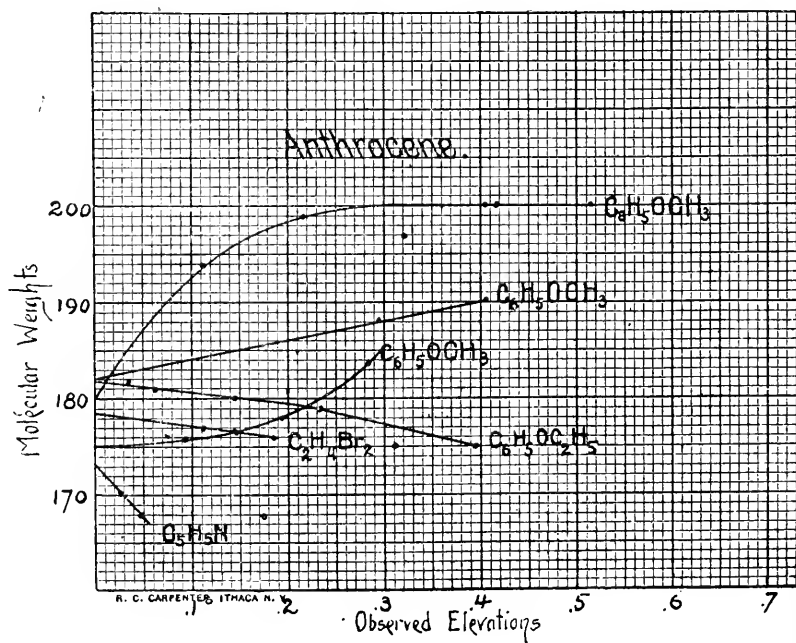
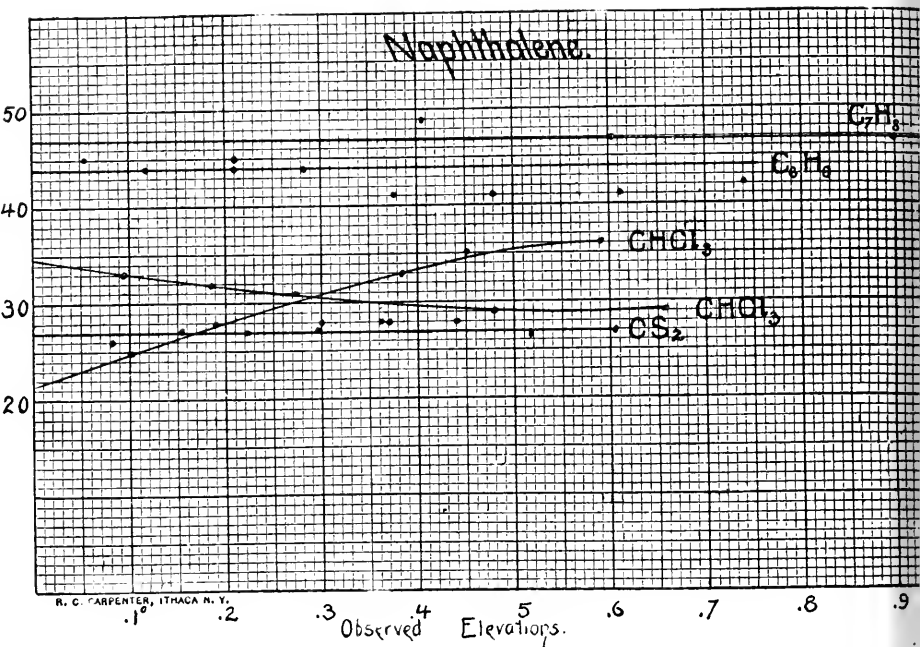
Molecular elevation for 100 grams, 60°.7.

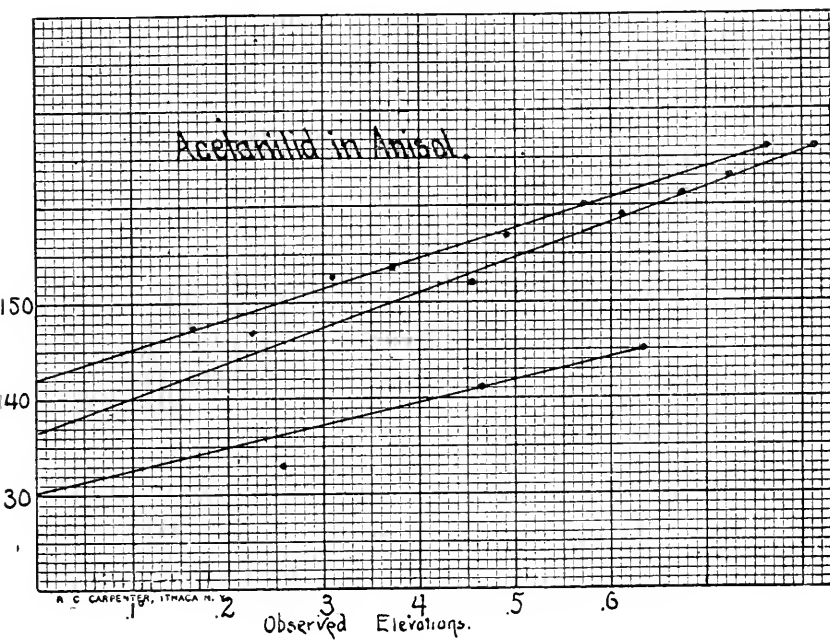
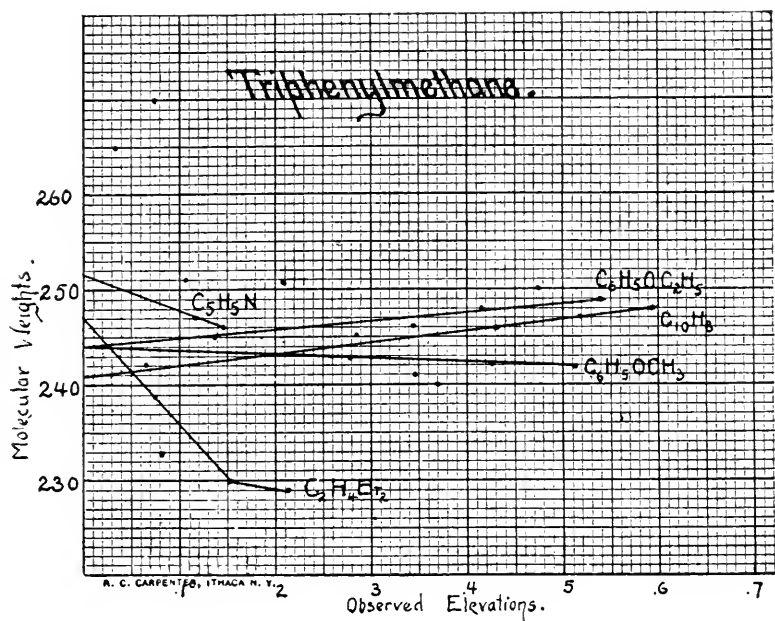
Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
89.75	0.2330	0°.065	61°.1	242
"	1.2315	0.346	61.5	241
"	1.5290	0.428	61.3	242
"	1.8554	0.508	60.0	247
"	2.1803	0.593	59.6	248
At infinite dilution,			61.5	241
Average of determinations,			60.7	244

Time, 40 minutes. Barometer, 735.7 mm. constant.

For the sake of completeness and to compare these results with those of others, they are here presented in a graphic form. The observed elevations are taken as abscissas and the molecular weights as ordinates. Each chart being for a single substance, with the solvents indicated by their formulas. The scales are so selected as to exaggerate the variations in the molecular weights.





GLUTARIMIDE.

BY R. SELDNER.

The reaction of Gautier¹ by which diacetamide is formed on heating acetonitrile and acetic acid together, has been applied to a number of other nitriles and monatomic acids, both of the fatty and of the aromatic series, by Colby and Dodge.² The results obtained showed the formation in most cases of mixed secondary amides. Miller³ has published the results of some experiments with succinic acid and its nitrile. He tried three different combinations; first, succinic acid and acetonitrile; second, succinic nitrile (ethylene cyanide) and acetic acid; and third, succinic acid with succinic nitrile. These three sets of experiments all gave the same product, succinimide.

It seemed to the writer desirable to try parallel reactions with glutaric acid, the next member of the series, and its nitrile. The glutaric nitrile was made by the method used by Fauconnier⁴ for preparing ethylene cyanide. A concentrated aqueous solution of potassium cyanide was slowly added to a boiling alcohol solution of trimethylene bromide. After boiling for some time, the alcohol and water were distilled off and the nitrile extracted from the dry residue with absolute alcohol. The alcohol was now evaporated under diminished pressure and the nitrile remaining was twice distilled *in vacuo*. It all distilled over between 150° and 180° at a pressure of 40 mm. and condensed to a clear, colorless liquid having a faint odor. To prepare glutaric acid, a portion of the nitrile was heated for some time with concentrated hydrochloric acid, and the solution finally evaporated to dryness. The impure glutaric acid was extracted from the dry residue with ether, decolorized with bone-black, and recrystallized from ether. It then formed clear, colorless prisms, melting at 98°. The acetonitrile used was purchased of Kahlbaum, Berlin, and was rectified over phosphorus pentoxide before use.

Three different combinations were made :

¹ Ztschr. Chem., 1869, 127.

² This Journal, 13, 1, (1891).

³ J. Am. Chem. Soc., 16, 443 (1894).

⁴ Bull. Soc. Chim. (Paris), 50, 214.

First Experiment.—6.6 grams of glutaric acid (1 molecule) and 4.1 grams of acetonitrile (2 molecules).

Second Experiment.—4.7 grams of glutaric nitrile (1 molecule) and 6.0 grams acetic acid (2 molecules).

Third Experiment.—6.6 grams glutaric acid and 4.7 grams glutaric nitrile (equal molecules).

The mixtures were introduced into strong glass tubes and 2 to 5 drops acetic anhydride added to each. The glass tubes were then sealed, placed in an oven, and heated. After heating for three hours at 180° , the contents of the tubes showed but little change. Four hours' further heating at 200° gave evidence of a reaction in the second and third tubes; they were therefore taken out and the first tube was heated five hours longer at 210° . All three tubes were now opened; slight pressure was noticed on opening. The contents were removed and washed with ether. The residues were then dissolved in alcohol, the solutions decolorized with bone-black, and concentrated to crystallization. The crystals obtained were recrystallized from alcohol and were then perfectly colorless and evidently pure. The amounts obtained from the three tubes were, respectively: first, 4.0 grams; second, 2.25 grams; and third, 5.4 grams. The crystals from the three tubes were identical in appearance. They formed thin square or rectangular plates with a fine lamellar cleavage.

The melting-points of the three sets of crystals were found to be:

I, at 153° ; II, at 152.8° ; III, at 152.5° .

The melting-point of glutarimide as given by Bernheimer¹ is 151° to 152° . Wolffenstein,² who obtained it by oxidizing piperidine with hydrogen peroxide, gives the melting-point as 154.5° .

The following elementary analyses were made:

Crystals I. 0.0780 gram substance gave 0.0430 gram H_2O and 0.1525 gram CO_2 .

Crystals II. 0.0774 gram substance gave 0.0432 gram H_2O and 0.1510 gram CO_2 .

Crystals III. 0.0989 gram substance gave 0.0548 gram H_2O and 0.1922 gram CO_2 .

¹ Gazz. chim. ital., **12**, 281.

² Ber. d. chem. Ges., **25**, 2777.

0.0995 gram substance gave 11.3 cc. N at 25° and 755.3 mm.

	I.	II.	III.	Theory for (CH ₂) ₃ ·(CO) ₂ ·NH.
C	53.32	53.20	53.00	53.10
H	6.13	6.20	6.16	6.19
N	12.57	12.39

The crystals were insoluble in ether and in benzene. An attempt was made to determine their molecular weight by Raoult's method, glacial acetic acid being used as solvent. The results obtained were very irregular.

10.6646 grams HC₂H₃O₂ used as solvent. With 0.0558 gram product dissolved, the freezing-point was lowered 0.1745°, corresponding to the molecular weight of 116.9.

With 0.1066 gram product dissolved the freezing-point was lowered 0.3425°, corresponding to the molecular weight of 113.8.

With 0.1564 gram product dissolved no constant freezing-point could be obtained, as the depression increased at each reading.

With 0.2060 and 0.2603 gram product in solution the freezing-point was also erratic.

The theoretical molecular weight for glutarimide is 113.

The products were further proved to be glutarimide by heating weighed quantities with concentrated hydrochloric acid, and determining the amounts of ammonia and glutaric acid formed. The ammonia was estimated by precipitation with platinic chloride.

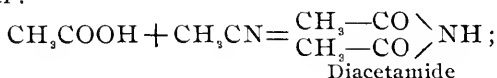
0.2001 gram substance gave 0.1681 gram Pt = 0.0293 gram NH₃; theory would require 0.0301 gram NH₃.

The glutaric acid was determined by evaporating to dryness, and exhausting the thoroughly dried residue with absolute ether. The ether was evaporated and the residue weighed after drying at 100°.

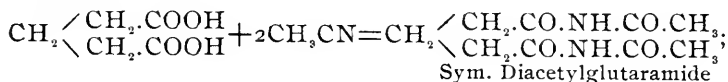
0.1974 gram substance gave 0.2274 gram glutaric acid; theory requires 0.2306 gram.

Glutarimide is therefore the principal product in all three experiments.

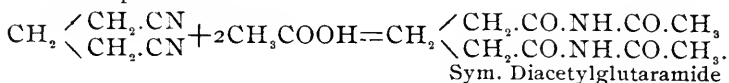
In experiment I, if the materials reacted parallel with those of Gautier:



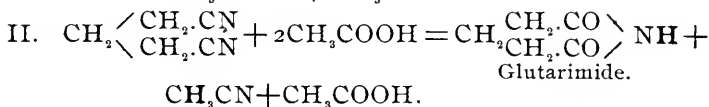
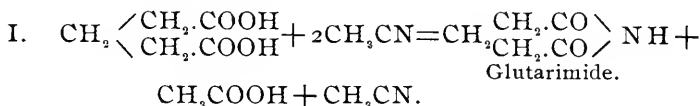
there would result :



and in experiment II :

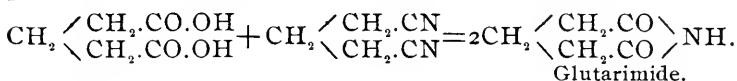


Since glutarimide was produced in large quantity in each tube, the reactions probably took place thus :



Acetic acid and acetonitrile are left over in both cases. These may have further reacted to form the diacetamide, $(\text{CH}_3\text{CO})_2\text{NH}$, of Gautier. To determine this point it is proposed to repeat these two experiments.

The best yield of glutarimide was obtained in the third experiment. The materials here have undoubtedly reacted thus :



It will be interesting to learn if other acids of the malonic series give imides on being heated with nitriles.

LABORATORY OF THE ADELPHI ACADEMY,
BROOKLYN, N. Y., March, 1895.

ON THE OXIDATION OF COMPLEX CARBOHYDRATES.

BY G. DE CHALMOT.

I recently advanced the hypothesis that in plants pentose molecules are formed in complex molecules of hexosans in which a part or all of the aldehyde groups have been bound by condensation, and are thereby preserved from further oxidation. It is probable that pentoses are formed from hexoses by the alcohol group at the end of the hexose molecule being

oxidized to aldehyde and carboxyl, and by the splitting off of carbon dioxide. I have since attempted to make in the laboratory pentosans from hexosans by making use of reactions similar to those which I suppose to take place in the walls of the plant-cells. These reactions are :

1. Oxidation to aldehyde of alcohol groups at the end of hexose groups which are united to complex carbohydrates.
2. Oxidation of these aldehyde groups to carboxyl.
3. Elimination of carbon dioxide from the carboxyl without affecting other parts of the hexose group.

The results which I have obtained concern only the first of these reactions. They are few and incomplete, for the work has been interrupted at an early stage. I shall, however, not return to the subject, and so communicate the results as they are.

Cross, Bevan, and Beadle¹ found that, if different complex carbohydrates, cane-sugar, milk-sugar, starch, cotton-cellulose, are oxidized with chromic acid, they are converted into compounds that yield furfurol, if they are heated with acids. I should not be surprised if these oxidized compounds contain glucuronic acid or its isomer. These compounds have, however, not been obtained in pure condition. I, therefore, sought for an oxidizing agent which would act gently and admit of obtaining oxidation-products of definite chemical composition. For this purpose I used bromine and soda, which have been used by E. Fischer for the oxidation of poly-acid alcohols. Fischer thus made *i*-galactose from dulcitol, and glycerose from glycerol.

The action of bromine and soda on starch, cane-sugar, cellulose, and α -methyl-*D*-glucoside was tested :

Starch.—5 grams of pulverized starch were mixed with a solution of 11 grams of soda in 60 cc. of water; 5 grams bromine were added and the mixture was shaken until the bromine was dissolved. In a short time carbon dioxide commenced to be given off. After an hour or more the liquid became entirely colorless. The mixture now reduced Fehling's solution in the cold; the starch had been partly liquified.

¹ Ber. d. chem. Ges., 26, 2523.

The mixture was neutralized with acetic acid, phenylhydrazine hydrochloride added, and the liquid heated on the water-bath. A slight precipitate of an osazone (?) was formed. The aldehyde reactions, which the starch showed after the treatment with bromine and soda, are due to an oxidation and to not hydrolysis, for bromine alone does not perceptibly act on starch in a week. After that time the mixture does not reduce Fehling's solution, not even if the starch has been liquified by boiling with water previous to being treated with bromine. Nor does soda alone act on starch.

Saccharose is also oxidized by bromine and soda, the solution becoming rapidly brown. However, if the solution is not too concentrated, the liquid can be obtained entirely colorless after the reaction is over. This liquid reduces Fehling's solution. Heated under proper conditions with phenylhydrazine, a small amount of osazone was precipitated in the liquid. This was glucosazone (melting-point: 202° ; percentage of nitrogen: 15.6).

5.5 grams of α -methyl-*d*-glucoside and 11 grams of soda were dissolved in 60 cc. of water; 5 grams of bromine were added to this solution, and dissolved by shaking. Reaction soon commenced: carbon dioxide was evolved and the liquid became colorless. This liquid reduced Fehling's solution slowly at the temperature of the room, at once at 50° ; the solution was neutralized with acetic acid, 5 grams of phenylhydrazine hydrochloride were added, and the liquid then heated on the water-bath. An osazone was precipitated. After cooling, this precipitate was collected. It weighed 0.7 gram. It was brown in color and contained, besides an osazone, at least one hydrazone or hydrazide. By repeated washings with small amounts of absolute alcohol, most of the impurities were removed and the osazone gradually became bright yellow. The osazone is nearly insoluble in cold alcohol. The hydrazone or hydrazide is red-brown, at least when precipitated in an impure condition by water from the alcoholic solution.

The osazone was recrystallized from boiling absolute alcohol. By longer boiling with alcohol, it seemed to be slightly decomposed. It was dried over sulphuric acid. The purest

acid, with dilute alkali, and with water, and dried. 5 grams were treated with 11 grams of soda and 5 grams of bromine. The reaction was slow, but, after some hours, the color of the bromine disappeared entirely. The cotton fibres retained their outer form. They were washed with water. They did not reduce Fehling's solution at the temperature of the room, but they reduced it at 100°. The cuprous oxide was precipitated on and in the fibres, which could be very nicely observed under the microscope. This cellulose thus showed one of the properties of the oxycelluloses of Cross, Bevan, and Beadle.¹ Further tests were not made.

SPRAY, NORTH CAROLINA.

ON THE DETERMINATION OF FORMIC ACID BY TITRATION WITH POTASSIUM PER- MANGANATE.

BY HARRY C. JONES.

Péan de Saint-Gilles² determined formic acid by titration with a standard solution of potassium permanganate in the presence of an alkaline carbonate. Lieben³ has shown that this titration can be carried to the end, satisfactorily, in the presence of the alkaline carbonate, the end being indicated by the appearance of color, due to the presence of a small quantity of unreduced permanganate. The principle is the same as that of Saint-Gilles, but the experimental work is more elaborate. Lieben states that the method has a slight drawback when the solution containing the formic acid is cold. The precipitate formed from the reduction of the permanganate does not settle quickly, and this renders it difficult to determine at once, whether the supernatant liquid is clear, or contains a trace of permanganate. It was found that by warming the solution on a water-bath, time was saved in determining the end of the reaction, without sacrificing the accuracy of the method. The method, as carried out by Lieben, seems to have yielded satisfactory results, yet it is well known that the color produced by a small amount of permanganate will gradually disappear if the solution stands in contact with the precip-

¹ Ber. d. chem. Ges., 27, 1061.

² Ann. chim. phys. [3], 55, 374, (1859).

³ Monatsh. Chim., 14, 746, (1893).

itated manganese hydroxide. This would render it difficult to determine always, the true end of the above reaction, especially when there is a large amount of formic acid present, giving rise to much of the manganese precipitate.

The method, which I employed in this laboratory for determining formic acid, does not differ in principle from the one above considered, but the procedure in making the titrations seems to be preferable to that employed by Lieben. The work in question was carried out in 1891, the same year in which Lieben states that he began his work along this line, in connection with an investigation suggested to the author by Prof. Remsen. The method is as follows: the solution containing the formic acid was made alkaline with sodium carbonate, warmed, and treated with an *excess* of a standard solution of potassium permanganate. All the formic acid was oxidized to carbon dioxide and water, and a heavy precipitate of manganese hydroxide was thrown down. The alkaline solution was then acidified with sulphuric acid, and a measured volume of oxalic acid run in until all the precipitate had dissolved, and all of the permanganate had disappeared. The excess of oxalic acid was finally titrated with a standard permanganate solution. A volume of oxalic acid, equal to that used, was then measured off, and titrated against the permanganate solution. The difference between the total permanganate used, and that amount which was equivalent to the oxalic acid, was the permanganate required to oxidize the formic acid. Knowing this, the amount of formic acid present was readily calculated.

To test the accuracy of this method a solution of pure formic acid was prepared, and the acid, in measured volumes, determined by the method just described. The results of these determinations showed that the solution contained the following percentages of formic acid :

Determination I.	Formic acid, 24.7 per cent.
“ II.	“ “ 24.9 “
“ III.	“ “ 25.1 “

The same solution of formic acid was then determined alkalimetrically, against a standard solution of potassium hydroxide, with the following results :

Determination I.	Formic acid, 25.1 per cent.
“ II.	“ “ 25.3 “

From the specific gravity, the formic acid present was 24.8 per cent.

Péan de Saint-Gilles¹ stated, further, that oxalic and formic acids can be determined in the presence of each other by means of potassium permanganate. The oxalic acid is oxidized by the permanganate in acid solution, while the formic acid is not acted upon under these conditions. The solution is then made alkaline with an alkaline carbonate; sodium carbonate and the formic acid determined by titration with more of the permanganate solution. This seemed to me to be rather doubtful from my own experience with these acids, and was subjected to experimental test. A weighed amount of oxalic acid was mixed with a large amount of formic acid and then an attempt was made to determine the oxalic acid by titration against a permanganate solution. The solution containing the mixture of the two organic acids was acidified with dilute sulphuric acid, and warmed just enough to facilitate the action of the permanganate on the oxalic acid.

0.3870 gram of oxalic acid was mixed with 2.4383 grams of formic acid in a dilute water solution. The oxalic acid found = 0.4235 gram.

0.7287 gram oxalic acid was brought into solution with a large excess of formic acid. The oxalic acid found = 0.9834 gram.

These results show that under these conditions some of the formic acid is also oxidized, and that oxalic acid cannot be determined by the method described by Saint-Gilles, if formic acid be present.

CHEMICAL LABORATORY.
JOHNS HOPKINS UNIVERSITY.

REVIEWS.

THEORETICAL CHEMISTRY. By PROF. WALTER NERNST, PH. D., of the University of Göttingen. TRANSLATED BY PROF. CHARLES SKEELE PALMER, PH. D., of the University of Colorado. With twenty-six wood cuts and two appendices. London and New York: Macmillan & Co., 1895. 697 pp. Price, five dollars.

When the original of this work on Theoretical Chemistry

¹ Ann. chim. phys. [3], 55, 374 (1859).

from the stand-point of Avogadro's Law and Thermodynamics appeared about two years ago in Germany, it was immediately recognized that a growing demand had been met by Dr. Nernst. The comprehensive *Lehrbuch* of Ostwald, while serving as *the text* for the specialist in physical chemistry, was too exhaustive for the average reader in this line. On the other hand, the *Grundriss*, by the same author, was too brief for those who wished to advance beyond the mere elements of the subject. The book in question, occupies a position intermediate between the two above mentioned, and serves as a guide through what may be termed the second stages of physicochemical study. In dealing with the subject from the standpoint of thermodynamics, the author brings out the important bearing of the study of energy transformations on physicochemical problems. An idea of the contents of this volume can be gained best by glancing at the subjects treated. Book I deals with the gaseous, liquid, and solid states of matter, with physical mixtures, and dilute solutions. Book II has to do chiefly with the atomic theory, the kinetic theory of the molecule, determination of molecular weights, the constitution of the molecule, physical properties and molecular structure, dissociation of gases, and electrolytic dissociation. Book III treats of the law of chemical mass-action, chemical statics, homogeneous and heterogeneous systems, chemical equilibrium in salt solutions, and chemical kinetics; while Book IV discusses thermochemistry, electrochemistry, and photochemistry. Two appendices are added in the translation, the first giving a brief account of the work done in physical chemistry during the year 1893, and the second is a table of chemical periodicals.

The growing interest in physical chemistry in America and England seems to demand the translation of such a work, and a translation has been furnished by Dr. Palmer. The reviewer regrets that a comparison of the translation with the original necessitates not a little adverse criticism of the work of the translator. The attempt "to combine fidelity to the original, with clearness in good English," if successful in reference to the former, leaves much to be desired in respect to the latter. Examples are only too numerous. On page 311, we find that "chemically equivalent quantities of the most *various* (verschiedene) ions are set free from the *most various* (verschiedenste) solutions;" on page 335, that an electrolyte is made up of "positive and negative *ingredients*" (Bestandtheile); on page 471, that "the saponification velocity, under conditions which are similar in other respects, is *actually proportional with very close approximation to*" (dass mit grosser Annäherung thatsächlich unter sonst gleichen Umständen die

Verseifungsgeschwindigkeit * * * proportional ist); on page 406 that "the relative depression of the vapor pressure, which is experienced by the solvent on adding a *strange* (fremde) substance;" on page 319 that "we may calculate *quite certainly* (sicher) the limiting value;" while on page 330 that "Arrhenius must be regarded as the *particular* (eigentlicher) father" of the dissociation theory, and the list could be extended much further.

Although the translation as a whole is unusually literal, yet erroneous translations are not wanting. On page 10 of the original we read, "Aeussere Arbeit, sowie kinetische Energie, bewegter Massen lässt sich auf mannigfache Weise und vollständig in einander überführen, sowie in Wärme verwandeln." In the translation, page 9, "external work," such as the kinetic energy of moving bodies may be transferred in many ways and completely into another form, as also into heat. On page 595 "Flüssigkeitsketten" is translated "liquid circuits," when liquid elements would have been less ambiguous. On page 648 it is stated that "Ramsay and Shields *insist, etc.*," while in the German we find "festsetzen." In many places, especially in the latter part of the book, the German word is given together with the English, indicating doubt in the mind of the translator, and in some cases such doubts could have been easily cleared up. Would it not have been better to give the nearest English equivalent, rather than fill the text with German words, since the translation is evidently for English readers?

It must, however, be remembered that it is no easy task to translate a book of this character, involving so many sides of physical chemistry, and written in a style which, though clear, is far from simple. The reader of this translation, who will overlook its shortcomings, will be able to obtain in most places a fair conception of what was meant by the author.

HARRY C. JONES.

ELEMENTARY QUALITATIVE CHEMICAL ANALYSIS, adapted for use in the Laboratories of Schools and Colleges. By FRANK CLOWES, D. Sc., (London), Professor of Chemistry in the University College, Nottingham, etc., and J. BERNARD COLEMAN, Senior Demonstrator of Chemistry in the University College, Nottingham, etc. Philadelphia: P. Blakiston, Son & Co., 1895.

Eleven pages of this book are devoted to use of apparatus, twenty to preparation and properties of oxygen, hydrogen, nitrogen, carbon dioxide, ammonia, chlorine, hydrochloric acid, distilled water, and nitric acid. The remaining 139 pages are devoted to qualitative analysis with free use of tables. The book seems neither better nor worse than dozens of others on

the same subject. Symbols are used everywhere instead of names. Prof. Clowes thinks this helpful to the student. It certainly is not agreeable to the average chemist to read a sentence like the following: "The solubility of PbSO_4 in $\text{H}\bar{\text{A}}$ and excess of AmHO ," or like this; "Mix some powdered $\text{Pb}\bar{\text{A}}_2 \cdot 3\text{H}_2\text{O}$ with about twice as much Na_2CO_3 in a cavity on a piece of charcoal." This book may, as Prof. Clowes thinks, supply a need in England, but why it should be republished in America is hard to understand, though only part of the great puzzle, Who uses the text-books on elementary qualitative analysis? A dozen new ones at least appear yearly, beside new editions of the old standards, and still new ones are written, differing in no marked way from the old, and—they find publishers.

E. R.

ANLEITUNG ZUR DARSTELLUNG CHEMISCHER ANORGANISCHER PRÄPARATE FÜR CHEMIKER UND PHARMAZEVTEN. VON DR. REINHART BLOCHMANN, Professor an der Universität Königsberg. Mit Abbildungen. Leipzig: Veit & Co., 1895.

This little volume gives minute directions for making 25 preparations. Dr. Blochmann has chosen preparations in which the raw materials are inexpensive, or are the products of preceding experiments. The length of time required, and variety in methods of work and forms of apparatus are also considered. The book can be recommended as clear, suggestive, and brief.

E. R.

QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES AS PRACTICED IN GEORGETOWN COLLEGE, D. C. New York: American Book Co., 1894.

This is a book of tables for elementary qualitative analysis, differing in some respects from those already in existence, but presenting no novel features calling for special notice.

E. R.

AMERICAN CHEMICAL JOURNAL.

INVESTIGATIONS ON THE SULPHONPHTHALEÏNS.¹

V.—ON SULPHONPHTHALEÏN AND SOME RELATED COMPOUNDS.

BY JOHN WHITE, JR.

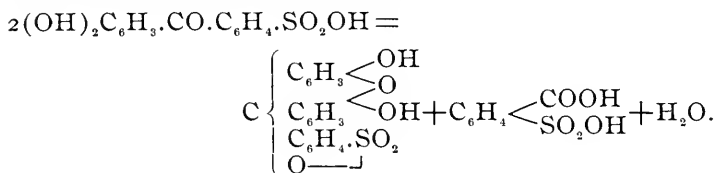
In order, if possible, to get further light on the nature of sulphonphtaleïn, I have undertaken at Professor Remsen's suggestion an investigation of some of its derivatives and of some related compounds. Great difficulties were encountered throughout the work, and the results are, therefore, not as satisfactory as could be desired. Still some facts of interest have been established, and a brief account of the work is herewith communicated.

Preparation of sulphonfluoresceïn from dioxybenzenesulphonic acid.—The method used was that described by Remsen and Linn.² The dioxybenzoylbenzenesulphonic acid was placed in a test-tube and heated in a sulphuric-acid bath. By means of a thermometer placed in the test-tube the temperature could be noted, and the mass could, at the same time, be stirred from time to time: a quite advantageous precaution, since, by frequent stirring, the reaction takes place much more rapidly. The temperature of the bath was allowed to rise gradually; at about 100°–110° the acid melts, the liquid thus formed being of a dark-red color; this rapidly becomes darker, and, when

¹ From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1891.

² This Journal, 11, 73.

the temperature is raised to 160°–170°, where the reaction takes place most readily, it becomes a deep brown; the mass meanwhile becomes quite viscous, and a considerable amount of water is given off. After heating for several hours the reaction is at an end. The mass was allowed to become cool, then was treated with cold water, and filtered. The sulphonfluoresceïn remaining on the filter was thoroughly washed with cold water to remove the orthosulphobenzoic acid formed as one of the products of the reaction:



It was then dissolved in alkalis, a moderately concentrated solution of caustic potash being used for this purpose. This solution is intensely fluorescent, even when extremely dilute, and is of a pale yellow color in transmitted light. The alkaline solution, after filtration, was treated with dilute acid, when the sulphonfluoresceïn was precipitated as a reddish-brown flocculent precipitate; this was washed a few times by decantation, then on the filter with the aid of the pump.

Sulphonfluoresceïn is very difficultly soluble in hot alcohol and in hot glacial acetic acid. It is more easily soluble in hot than in cold water, though but slightly soluble in either. It dissolves with great ease in alkalis, forming the intensely fluorescent solutions spoken of above.

Action of bromine on sulphonfluoresceïn.—Von Baeyer¹ found that when fluoresceïn is treated with bromine, three substitution-products are obtained, according to the proportion of bromine used: monobromfluoresceïn, dibromfluoresceïn, and tetrabromfluoresceïn (eosin). He was unable to obtain the tribromfluoresceïn. Of these he only succeeded in isolating in pure condition the dibrom- and tetrabromfluoresceïns, and from the latter a number of well-defined salts were obtained.

In the case of sulphonfluoresceïn, the principal action of bromine is to form the *dibromsulphonfluoresceïn*, and probably

¹ Ann. Chem. (Liebig), 183, 36.

a *monobromsulphonfluoresceïn*. The tribrom- and tetrabrom-substitution-products could not be obtained. Dry sulphonfluoresceïn was suspended in four or five times its weight of glacial acetic acid in a small beaker; to this was added a twenty-per cent. solution in glacial acetic acid, in the proportion of one molecule of bromine to one of sulphonfluoresceïn. Reaction immediately took place, the liquid becoming warm from the reaction, and fumes of hydrobromic acid being given off. A solid product was thus obtained, somewhat lighter in color than the original sulphonfluoresceïn. It was filtered off, washed with glacial acetic acid, in which it is much less soluble than in water, and placed in a desiccator containing solid caustic potash to remove the last traces of acetic acid. The bromine product is slightly soluble in alcohol and water. It is insoluble in ether, chloroform, glacial acetic acid, and petroleum-ether. In alkalis it dissolves readily, forming strongly fluorescent solutions, which show a very decided pink in transmitted light, very similar to that produced by eosin. Estimations of sulphur and bromine gave the following results :

I. 0.1195 gram substance gave 0.0550 gram BaSO_4 (Liebig).

II. 0.1596 gram substance gave 0.0782 gram AgBr (Carius).

	Calculated for $\text{C}_{19}\text{H}_{11}\text{BrO}_6\text{S}$.	Found.
S	7.17	6.32
Br	17.88	20.85

It was concluded from these results that some dibromsulphonfluoresceïn had been formed at the same time as the monobrom-product, and that a mixture of the two was thus obtained. It was then decided to prepare other bromine substitution-products of sulphonfluoresceïn to see if some of these could be obtained in pure condition.

With this in view, sulphonfluoresceïn was treated with two molecules of bromine in the manner described above. The action was in every respect similar to that described in the preceding experiment, except that in this case, after standing for a short time, the whole mass became almost solid, and the reaction appeared to take place more readily than in the previous case. The product obtained was much like that obtained in the first experiment, but appeared to be more gran-

ular, and was hence easier to wash. The following analyses were obtained:

- I. 0.1187 gram substance gave 0.0526 gram BaSO_4 (Liebig).
- II. 0.0772 gram substance gave 0.0509 gram AgBr (Carius).
- III. 0.0903 gram substance gave 0.0600 gram AgBr (Carius).
- IV. 0.29685 gram substance, heated for three hours at 160° , lost 0.00951 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{10}\text{Br}_2\text{O}_6\text{S}+\text{H}_2\text{O}$.	I.	II.	Found. III.	IV.
S	5.89	6.09
Br	29.39	28.06	28.27
H_2O	3.30	3.20

The bromine in this product is somewhat lower than that required for dibromsulphonfluoresceïn, and further experiments in this line failed to give a pure dibromine product.

Three molecules of bromine were next added to one molecule of sulphonfluoresceïn. The action took place as in previous experiments. Estimations of sulphur and bromine gave the following results:

- I. 0.1240 gram substance gave 0.0504 gram BaSO_4 (Liebig).
- II. 0.0919 gram substance gave 0.0611 gram AgBr (Carius).

	Calculated for $\text{C}_{19}\text{H}_9\text{Br}_3\text{O}_6\text{S}$.	Calculated for $\text{C}_{19}\text{H}_{10}\text{Br}_2\text{O}_6\text{S}+\text{H}_2\text{O}$.	I.	Found. II.
S	5.30	5.89	5.59
Br	39.65	29.39	28.29

Another product was prepared by treating sulphon-fluoresceïn with four molecules of bromine. Reaction took place at once, with copious evolution of fumes of hydrobromic acid.

An analysis of the product gave the following figures:

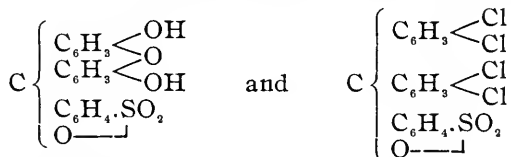
- I. 0.1810 gram substance gave 0.2883 gram CO_2 and 0.0476 gram H_2O .
- II. 0.2768 gram substance gave 0.4293 gram CO_2 and 0.0733 gram H_2O .
- III. 0.1325 gram substance gave 0.0533 gram BaSO_4 (Liebig).
- IV. 0.2175 gram substance gave 0.0918 gram BaSO_4 (Liebig).
- V. 0.0703 gram substance gave 0.0466 gram AgBr (Carius).

	Calculated for $C_{19}H_{10}Br_2O_6S+H_2O$.	I.	II.	Found. III.	IV.	V.
C	41.91	43.44	42.30
H	2.21	2.93	2.94
Br	29.39	28.21
S	5.89	5.52	5.76

It appears probable, from a consideration of the results obtained, that the principal product of the action of bromine on sulphonfluoresceïn is a *dibromsulphonfluoresceïn*, but that, owing to the difficulty attending the separation of the products formed in the reaction, it cannot be obtained in pure condition. The dibrom substitution-product may be mixed with one or more of the other bromine products, or perhaps the action is not complete, and this appears to be shown by the fact that the analyses for bromine, while agreeing very well for the various preparations, are too low in all cases; the carbon and hydrogen are likewise too high.

The action of *acetic anhydride* on dibromfluoresceïn gave a product insoluble in alkalis, and, therefore, probably an acetyl derivative. The analyses of this product did not, however, give figures agreeing with any probable formula.

Phosphorus pentachloride acts upon sulphonfluoresceïn readily at 125° – 130° , giving rise to the formation of a product, with a bright red color, soluble to some extent in alcohol and in alkalis. The solution in alkalis first assumes a deep cyanide-blue color which, upon standing, soon changes to green, then to pale yellow, and finally becomes colorless. The analyses gave figures which showed that the substance was an impure tetrachlorine product, the relation of which to the fluoresceïn is probably expressed by these formulas:



Action of Resorcinol on Orthosulphobenzoic Acid.—The preparation of sulphonfluoresceïn by heating dioxybenzoylbenzenesulphonic acid involves a splitting off of orthosulphobenzoic acid (see equation, p. 546). It was thought that, by mixing the dioxy acid with resorcinol a larger yield of sulphonfluor-

esceïn might be obtained. It was found, however, that at least two products were formed, one of which was sulphonfluoresceïn, the other or others resulting in all probability from the action of the resorcinol on the orthosulphobenzoic acid. Hence, experiments were made on the action of these two substances upon each other. Fahlberg and Barge,¹ describe some experiments performed by them on the action of resorcinol on orthosulphobenzoic acid. They found that when orthosulphobenzoic acid is heated with either 2 or 4 molecules of resorcinol, a condensation-product is obtained containing four resorcinol residues. They ascribe to it the formula $C_{31}H_{20}O_8S + 4H_2O$, and give the following analyses :

	Calculated for $C_{31}H_{20}O_8S + 4H_2O$.	I.	II.	Found.	III.	IV.
C	59.60	59.12	59.04	59.68
H	4.50	4.97	4.91
S	5.13	5.24	5.05	5.38	5.34	5.34
H ₂ O	11.54	11.42	11.20	11.38	11.38

As there were very few or no details given and no further investigation made, it seemed desirable, especially since it is in line with the series of investigations which have been carried on in this laboratory for some years past, to repeat the work of Fahlberg and Barge, and also to see if other phenol residues might be introduced in the same way.

I.—Orthosulphobenzoic acid and resorcinol (1:4) were heated together in a sulphuric-acid bath. The temperature was allowed to rise gradually; at 100°–110° the mixture melted to a deep-red liquid, which gradually grew darker as the temperature rose. At 140° reaction took place, bubbles were seen to pass up through the liquid, water was given off, and in the course of a few hours the mass became quite viscous and dark in color. The product thus obtained was, when cold, hard, quite brittle, and of a reddish-brown color, somewhat different from that of sulphonfluoresceïn. The physical properties of the substance are worthy of comment. When rubbed it shows electrical phenomena; when treated with water in the cold it softens to a slight extent, then becomes hard again, the process being similar to the setting of plaster of Paris or of cement; this is even more noticeable if it is

¹ Ber. d. chem. Ges., 22, 765.

heated with water. At the boiling-point of water it is a soft, dark-green mass, of the consistency of tar, and floats on the surface of the water. Upon cooling the mass becomes hard and brittle and sinks in the water. When the mass is heated in an air-bath to a temperature of 120° the same phenomenon is noticed. This change in physical condition does not appear to be attended by any change in chemical composition. The substance dissolves quite readily in alkali, forming an intensely fluorescent solution, but the fluorescence is of a different character from that of sulphonfluoresceïn. The solution is of a deep-red color in concentrated form, showing a delicate pink in dilute form, while, as before stated, sulphonfluoresceïn shows a yellow color in dilute solution.

It is precipitated from the alkaline solution by acids, and for purposes of purification this method was used. The precipitate is flaky, and very difficult to wash thoroughly. After purification it was carefully examined. It is easily soluble in alcohol and ether, insoluble in chloroform, water, petroleum-ether, and in cold glacial acetic acid, slightly soluble in warm. Analysis gave the following results :

I. 0.2231 gram substance gave 0.5281 gram CO_2 and 0.0990 gram H_2O .

II. 0.1703 gram substance gave 0.0428 gram BaSO_4 (Liebig).

III. 1.2564 grams substance, heated for four hours at 140° , lost 0.0788 gram H_2O .

IV. 0.6253 gram substance, heated for five hours at 140° , lost 0.0404 gram H_2O .

V. 0.1712 gram substance gave 0.4054 gram CO_2 and 0.0706 gram H_2O .

VI. 0.7668 gram substance, heated for four hours at 140° , lost 0.0384 gram H_2O .

VII. 0.2790 gram substance, heated for five hours at 140° , lost 0.0156 gram H_2O .

	Calculated for $\text{C}_{31}\text{H}_{20}\text{O}_8\text{S} + 4\text{H}_2\text{O}$. (Fahlberg and Barge.)	Calculated for $\text{C}_{43}\text{H}_{28}\text{O}_{10}\text{S} + 3\frac{1}{2}\text{H}_2\text{O}$.
C	59.60	64.57
H	4.50	4.39
S	5.13	4.01
H_2O	11.54	7.88

	I.	II.	III.	Found. IV.	V.	VI.	VII.
C	64.56	64.59
H	4.93	4.58
S	3.45
H ₂ O	6.27	6.46	5.01	5.59

Four other sulphur-estimations gave respectively 4.26, 3.97, 4.11, and 4.24 per cent.

The results of all my analyses point to the conclusion that orthosulphobenzoic acid and resorcinol react under the conditions above described to form a product containing six residues of resorcinol united to one of the acid. Accordingly experiments were next made in which the substances were mixed in the proportion of 1 molecule of the acid to 6 of resorcinol. The analyses of the products gave the following results:

Preparation I.

I. 0.2176 gram substance gave 0.5177 gram CO₂ and 0.0944 gram H₂O.

II. 0.1345 gram substance gave 0.0362 gram BaSO₄ (Liebig).

III. 1.3625 grams substance, heated for four hours at 140°, lost 0.0820 gram H₂O.

Preparation II.

I. 0.2655 gram substance gave 0.0752 gram H₂O (combustion).

II. 0.1744 gram substance gave 0.0436 gram BaSO₄ (Liebig).

III. 1.2358 grams substance, heated for four hours at 140°, lost 0.0675 gram H₂O.

Preparation III.

0.2559 gram substance gave 0.6115 gram CO₂ and 0.1153 gram H₂O.

	Calculated for C ₄₃ H ₂₈ O ₁₀ S+3½H ₂ O.	Prep. I.			Found.			Prep. III.
		I.	II.	III.	I.	II.	III.	
C	64.57	64.93	65.17
H	4.39	4.82	4.98	5.01
S	4.01	...	3.70	3.44
H ₂ O	7.88	6.02	5.46	...

It will be observed that in all cases the estimations of water of crystallization are low. An explanation of this will be offered later.

The results obtained do not agree as well as could be wished, but, considering the nature of the substance and the difficulty attending its purification, this is not surprising.

Since it was difficult to decide between several formulas—some containing six resorcinol residues, with varying amounts of water of crystallization; others containing four resorcinol residues, but which contain much less water than that ascribed to it by Fahlberg and Barge—it seemed desirable to analyze the dehydrated substance, as the differences between the tetra- and hexaresorcinol derivatives are more marked. After heating for several hours at 140° , the residues were analyzed:

Product I_4^1 .

I. 0.1188 gram substance gave 0.2966 gram CO_2 and 0.0587 gram H_2O .

II. 0.1320 gram substance gave 0.3317 gram CO_2 and 0.0569 gram H_2O .

III. 0.1130 gram substance gave 0.0285 gram $BaSO_4$ (Liebig).

IV. 0.1374 gram substance gave 0.0364 gram $BaSO_4$ (Liebig).

Product II_4 .

I. 0.1393 gram substance gave 0.3462 gram CO_2 and 0.0542 gram H_2O .

II. 0.1018 gram substance gave 0.0302 gram $BaSO_4$ (Liebig).

III. 0.1258 gram substance gave 0.0398 gram $BaSO_4$ (Liebig).

Product III_6 .

I. 0.1224 gram substance gave 0.3078 gram CO_2 and 0.0439 gram H_2O .

II. 0.1208 gram substance gave 0.0289 gram $BaSO_4$ (Liebig).

Product IV_6 .

I. 0.1379 gram substance gave 0.3459 gram CO_2 and 0.0566 gram H_2O .

¹ The small figures 4 and 6 refer to the preparations made by using 4 and 6 molecules respectively of resorcinol.

II. 0.1195 gram substance gave 0.0283 gram BaSO_4 (Liebig).

III. 0.1492 gram substance gave 0.0353 gram BaSO_4 (Liebig).

On comparing these results with those calculated for substances containing 4 and 6 residues of resorcinol, the following table will show that they are more in accord with those required by a substance containing 6 such residues:

	Calculated for $\text{C}_{31}\text{H}_{20}\text{O}_8\text{S}$ (4 Resorcin).	Calculated for $\text{C}_{43}\text{H}_{28}\text{O}_{10}\text{S}+\text{H}_2\text{O}$ (6 Resorcin).	Prep. I ₄ .		Found. Prep. II ₄ .		Prep. III ₆ .	Prep. IV ₆ .	
			I.	II.	I.	II.		I.	II.
C	67.38	68.41	68.10	68.62	67.78	...	68.58	68.41	...
H	3.63	3.98	5.49	4.79	4.33	...	3.99	4.56	...
S	5.80	4.25	3.47	3.64	4.08	4.34	3.29	3.26	3.25

It appears from this that all the water of crystallization is not driven off at 140° , but that there still remains 1 molecule. This explains the low results in the previous determinations of water, for it will be seen from a study of those results that the difference between the percentages found and the calculated is just about what is required for 1 molecule of water. An attempt was made to drive off this last molecule of water. The temperature of the air-bath was allowed to rise gradually above 140° , and weighings made from time to time showed a gradual loss in weight. When a temperature of 180° was reached a surprising observation was made. On removing the weighing-tube containing the substance from the bath, a strong odor of sulphuretted hydrogen was noticed. A test was made with silver nitrate and with lead acetate solutions, and both gave the characteristic reactions for hydrogen sulphide. This was an entirely unaccountable decomposition, and one for which no explanation can be offered.

Taking all the facts into consideration, it appears that the subject is an extremely difficult one to deal with, owing to the nature of the substance, the difficulties attending its purification and separation from other substances of like kind, and the peculiar behavior under the influence of heat. It may be said, however, that the facts point to the conclusion that when orthosulphobenzoic acid is heated with either 4 or 6 molecules of resorcinol, a condensation-product containing *six* resorcinol residues is obtained.

With the desire to determine if the hexaresorcinol-derivative of orthosulphobenzoic acid is the only product of the action of resorcinol on the acid, an experiment was made in which a smaller proportion of resorcinol was used than in the preceding experiments. In this case only 2 molecules of resorcinol were used. The experiment was performed in a manner entirely similar to the preceding, and the product obtained had the same general appearance and similar properties to that previously described. Upon making an analysis, however, it was soon apparent that this was a different substance, thus :

I. 0.1690 gram substance gave 0.4060 gram CO_2 and 0.0671 gram H_2O .

II. 0.1701 gram substance gave 0.0697 gram BaSO_4 (Liebig).

III. 0.3434 gram substance, heated for four hours at 150° , lost 0.0101 gram H_2O .

The figures thus obtained agree very closely with those calculated for a product containing *four* resorcinol residues, but containing less water than that described by Fahlberg and Barge :

	Calculated for $\text{C}_{31}\text{H}_{20}\text{O}_8\text{S}+4\text{H}_2\text{O}$ (Fahlberg and Barge).	Calculated for $\text{C}_{31}\text{H}_{20}\text{O}_8\text{S}+\text{H}_2\text{O}$.		Found.	
			I.	II.	III.
C	59.60	65.24	65.52
H	4.50	3.86	4.42
S	5.13	5.62	...	5.63	...
H_2O	11.54	3.16	2.94

In regard to the constitution of the tetraresorcinol derivative as well as of the hexa derivative, it seems idle at present to speculate. It is, of course, quite possible to assign places to the resorcinol residues in the molecule, but the experimental data are not as yet sufficient to make that kind of speculation profitable.

Summary.

It appears from the foregoing :

1. That when sulphonfluorescein is treated with bromine, the chief product of the action is the formation of a dibromine substitution-product.

2. That phosphorus pentachloride causes the substitution of chlorine for the two hydroxyl groups and for the anhydride oxygen in sulphonfluorescein.

3. It is not possible to prepare sulphonfluorescein by the action of resorcinol on orthosulphobenzoic acid, but when action takes place between these 2 substances, either 4 or 6 residues of resorcinol enter into the combination according to the circumstances.

VI.—SULPHONPHTHALEINS DERIVED FROM ORTHOSULPHOPARATOLUIC ACID.¹

BY WALTER JONES.

The starting-point in these experiments was methylsaccharin that had been placed at the disposal of Professor Remsen by the "Badische Anilin- und Soda-fabrik."² The methylsaccharin was first converted into the corresponding acid ammonium salt by boiling it with dilute hydrochloric acid.

For the purpose of preparing methyldioxybenzoylbenzenesulphonic acid the finely powdered, dry salt is placed with resorcinol (1 mol. acid to 2 mols. resorcinol) in a large test-tube which is in turn immersed in a bath of sulphuric acid. The temperature of the bath is gradually raised, while the contents of the tube are continually stirred with a thermometer. At 100° the resorcinol melts to a dark-red liquid, and the ammonium salt sinks to the bottom. At 160° the ammonium salt dissolves, but no reaction takes place until the temperature rises above 185°. By heating at this temperature for a few minutes, a bubbling begins, due to the escape of water formed in the reaction, and a yellow line is seen on the side of the tube where the thermometer touches in stirring. The entire liquid soon becomes a paste of yellow crystals, and if the stirring be now discontinued, no further reaction can be made to take place, however long the heating be continued, but by stirring the viscous material for about fifteen minutes it becomes almost solid. The whole process requires about forty minutes if the stirring is not stopped, this being a necessary condition for the completion of the reaction.

After cooling, the light-yellow crystalline mass is extracted with water, and the dark-red solution thus obtained is filtered. On evaporating and cooling the solution, a poorly crystalline

¹ From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1891.

² See also Randall: *This Journal*, 13, 256; and Lyman: *Ibid.* 16, 513.

yellow material is deposited, and the mother-liquor contains a viscous substance which prevents any further deposition upon subsequent evaporation. If, however, alcohol is added, a further yield may be obtained. The yellow color may be removed from the crystals by boiling the water-solution with animal charcoal and crystallizing repeatedly; but a more convenient way is to treat the yellow material with successive small portions of cold alcohol, in which the coloring-matter is easily soluble, and a separation can thus be effected by filtration. By dissolving the colorless material thus obtained in a large excess of hot alcohol, and allowing the solution to evaporate slowly, crystals of considerable size and of great perfection can be obtained. As this process involves a loss by creeping, and as the supply of material at hand was limited, a saturated water-solution of the salt was placed in a sulphuric-acid desiccator and small crystals thus gradually obtained. The analysis of these crystals gave the following results:

0.2955 gram salt gave 0.1246 gram H_2O and 0.5626 gram CO_2 .

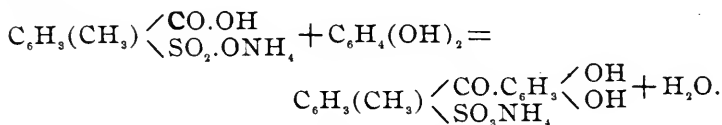
0.3910 gram salt gave 0.1663 gram H_2O and 0.7400 gram CO_2 .

0.2364 gram salt gave 0.1695 gram $BaSO_4$.

0.2713 gram salt gave 0.1959 gram $BaSO_4$.

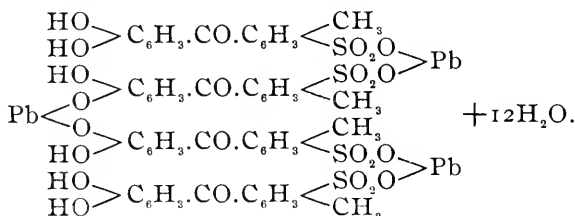
	Calculated for $C_{14}H_9SO_6N$.	I.	II.	Found.		V.	VI.
				III.	IV.		
C	51.67	51.92	51.61
H	4.63	4.69	4.73
S	9.86	9.85	9.92
N	4.32	4.19	4.20

These analyses show that the reaction which gave rise to this compound must have taken place according to this equation:



The existence of a basic lead salt of dioxybenzoylbenzenesulphonic acid, which is quite insoluble in water, suggested the corresponding salt of this acid as a possible means of ob-

taining the acid itself. A water-solution of the ammonium salt was boiled with finely powdered minium. The solution should be concentrated and the vessel open to allow an escape of ammonia, otherwise the reaction is very slow. The basic lead salt thus formed is light, and can be almost completely separated from the excess of minium by decantation, the latter being heavy and adhering to the bottom and sides of the vessel. The decanted liquid, which contains an amount of the ammonium salt, is filtered off, and the precipitate obtained on the filter has a light flesh color, owing doubtless to the inclusion of traces of finely-powdered lead oxide. If, however, the material is dissolved in dilute acetic acid and boiled with animal charcoal, large colorless crystals can be obtained without difficulty. Although the solution in acetic acid has always a red color, yet the salt deposited from the concentrated solution is colorless, and as the deposition continues the solution itself gradually loses its color. The salt loses 11 molecules of water at 105° , and a twelfth at 135° , and the completely dehydrated material has a yellow color. The analysis of this salt is in accordance with the formula given below, and as no other formula can be suggested that will accord so well as this one with the analytical results obtained, it has been thought extremely probable:



The lead was determined by igniting in a porcelain crucible with sulphuric acid. The analytical results are as follows:

0.3163 gram of the salt gave 0.0298 gram H_2O at 105° , 0.0330 gram H_2O at 135° , and 0.1396 gram PbSO_4 .

0.4736 gram of the salt gave 0.0440 gram H_2O at 105° , 0.0504 gram H_2O at 135° , and 0.2072 gram PbSO_4 .

0.6015 gram of the salt gave 0.0567 gram H_2O at 105° , 0.0625 gram H_2O at 135° , and 0.2654 gram PbSO_4 .

	Calculated.	I.	Found. II.	III.
11 H ₂ O	9.60	9.42	9.29	9.43
12 H ₂ O	10.47	10.43	10.64	10.39
Pb	30.08	30.14	29.88	30.13

When all the acetic-acid mother-liquors were brought together they were boiled with lead oxide for the purpose of getting rid of the large excess of acetic acid present. The basic lead salt was decanted as before, but on filtering off the liquid there separated from the filtrate, as it touched the cold flask, a yellow powder in considerable quantity. This powder was found to be soluble in hot water but could not be crystallized from the solution, always falling as a fine crystalline powder when the solution cooled. The salt loses its water of crystallization so easily that it was found impossible to determine it, and the lead determinations were made from the completely dehydrated salt. The analyses given below correspond to the composition represented by the formula



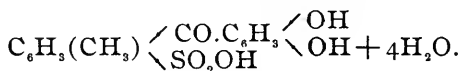
0.3408 gram of the salt gave 0.2828 gram PbSO₄.

0.2163 gram of the salt gave 0.1797 gram PbSO₄.

	Calculated.	I.	Found. II.
Pb	56.22	56.66	56.73

It was difficult to obtain the acid in pure condition, owing to its extreme solubility in water. Alcohol was tried, but with no more successful result. A solution of the pure basic lead salt, in as little acetic acid as would dissolve it, was completely precipitated with sulphuretted hydrogen, and the lead sulphide filtered off. The solution was then evaporated almost to dryness before any crystallization took place, and the material had a decidedly reddish-brown color, due probably to decomposition caused by the continued heating which was necessary to expel the last traces of acetic acid. In order to avoid the use of acetic acid, some of the pure basic lead salt was ground fine in an agate mortar, and sulphuretted hydrogen passed through a suspension of the powder in water. After the lead sulphide had been filtered off the solution was evaporated, as before, on a water-bath. When the liquid be-

came viscous, spherical aggregates began to separate, and the heating was discontinued. After the material had stood for a few days, the vessel contained a solid mass of beautifully crystalline acid, and on the sides of the vessel was a most delicate pink tinge. The liquid acid which was allowed to stand for crystallization was of a light straw color, but the crystals were colorless. The easy decomposition of this acid by heat prevented accurate determinations of its water of crystallization. The analysis, however, for carbon, hydrogen, and sulphur showed that it has the formula



0.1227 gram acid gave 0.0757 gram BaSO_4 .

0.2279 gram acid gave 0.1418 gram BaSO_4 .

0.1416 gram acid gave 0.0646 gram H_2O and 0.2294 gram CO_2 .

0.1319 gram acid gave 0.0586 gram H_2O and 0.2158 gram CO_2 .

	Calculated.	Found.			
		I.	II.	III.	IV.
S	8.44	8.48	8.55
C	44.20	44.50	44.62
H	5.27	5.11	4.94

Barium Salt, $\left(\text{C}_6\text{H}_5(\text{CH}_3) \begin{matrix} \diagup \text{CO} \cdot \text{C}_6\text{H}_5 \diagdown \text{OH} \\ \diagdown \text{SO}_2 \diagup \end{matrix} \right)_2 \text{Ba} + 5\text{H}_2\text{O}.$ —

This salt crystallizes from its water solution in small but well defined crystals. When the crystallization occurs from a very concentrated solution, the crystals form spherical aggregates having a beautiful satin lustre when broken. In an experiment, which will be described later, some crystals of this salt were obtained of a size which would admit of measurement. When examined under the microscope two forms could be clearly distinguished. The large crystals seemed to have rhombohedral faces, while the small radially concentric tufts appeared as tetragonal prisms. As the faces were mottled by impurity unequally distributed, and besides very much curved, no measurements were made. The analysis of the salt gave the following results:

0.2866 gram of the salt gave off 0.0315 gram H_2O and yielded 0.0786 gram BaSO_4 .

0.2721 gram of the salt gave off 0.0298 gram H_2O and yielded 0.0748 gram BaSO_4 .

0.1943 gram of the salt gave off 0.0207 gram H_2O .

	Calculated.	I.	Found. II.	III.
$5\text{H}_2\text{O}$	10.70	11.00	10.98	10.65
Ba	16.30	16.13	16.17

Calcium Salt, $\left(\text{C}_6\text{H}_3(\text{CH}_3) \begin{smallmatrix} \diagup \text{CO} \cdot \text{C}_6\text{H}_3(\text{OH})_2 \\ \diagdown \text{SO}_3 \end{smallmatrix}\right)_2 \text{Ca} + 6\text{H}_2\text{O}$.—

This salt forms a crystalline mass.

0.3303 gram of the salt gave off 0.0452 gram H_2O and yielded 0.0591 gram CaSO_4 .

0.2791 gram of the salt gave off 0.0374 gram H_2O and yielded 0.0494 gram CaSO_4 .

	Calculated.	I.	Found. II.
$6\text{H}_2\text{O}$	14.19	14.00	13.88
Ca	5.25	5.26	5.24

Neutral Lead Salt, $\left(\text{C}_6\text{H}_3(\text{CH}_3) \begin{smallmatrix} \diagup \text{CO} \cdot \text{C}_6\text{H}_3(\text{OH})_2 \\ \diagdown \text{SO}_3 \end{smallmatrix}\right)_2 \text{Pb} + 7\text{H}_2\text{O}$.—The easy formation of two perfectly stable basic lead salts by heating a solution of the ammonium salt with lead oxide would lead to the belief that these are the forms in which lead would be likely to occur in combination with this acid. Yet when a warm-water solution of the acid is treated with lead carbonate, the compound formed is the neutral lead salt, which shows no tendency to pass over into either of the basic salts even when its solution is boiled. The salt cannot be obtained in definite crystal forms, owing to its easy solubility in water, but separates as a gelatinous paste from extremely concentrated solutions. This paste, however, is easily soluble in water, showing that no conversion has taken place into either of the basic salts.

0.2871 gram salt gave 0.0386 gram H_2O and 0.0937 gram PbSO_4 .

0.2246 gram salt gave 0.0296 gram H_2O and 0.0737 gram PbSO_4 .

	Calculated.	Found.	
		I.	II.
7H ₂ O	13.30	13.47	13.19
Pb	21.85	22.29	22.40

Zinc Salt, $(C_6H_5(CH_3) \begin{smallmatrix} \diagup CO.C_6H_5(OH)_2 \\ \diagdown SO_3 \end{smallmatrix})_2 Zn + n.H_2O. -$

This salt could only be separated from its water solution by drying for a long time in a sulphuric-acid desiccator. The material thus obtained did not contain water of crystallization, although this might have been lost in the process of drying. The substance which was analyzed was of a dark red color and probably partly decomposed, yet the material contained just the amount of zinc required to form a zinc salt of this acid.

0.1969 gram of the salt gave 0.0463 gram ZnSO₄.

0.2489 gram of the salt gave 0.0592 gram ZnSO₄.

	Calculated.	Found.	
		I.	II.
Zn	9.60	9.51	9.62

Silver Salt, $C_6H_5(CH_3) \begin{smallmatrix} \diagup CO.C_6H_5(OH)_2 \\ \diagdown SO_3Ag \end{smallmatrix} + 2H_2O. -$ Con-

siderable difficulty was experienced in preparing this salt, owing to its sensitiveness to light. It can be made to crystallize in fine large crystals if the solution is concentrated on a water-bath, but the heating necessary for this evaporation always turns the liquid a dark color. A specimen of the salt prepared by treating a cold water solution of the acid with pure silver carbonate was placed in a desiccator and protected from the light. Although the utmost care was taken to prevent decomposition of the salt, nevertheless the liquid soon became dark, and it was thought advisable to remove the few colorless crystals that had formed. The water of crystallization is given off on exposure to the air, some of the small crystals having lost their lustre at the beginning of the analysis. The silver was determined as the metal by igniting the salt and then evaporating with nitric acid.

0.1528 gram salt gave 0.0118 gram H₂O and 0.0365 gram Ag.

	Calculated.	Found.
2H ₂ O	7.98	7.72
Ag	23.93	23.90

The free acid was treated with acetic anhydride, but even at the boiling temperature of the anhydride no transformation into an acetyl product could be effected.

When the free acid is treated with phosphorus pentachloride, even as high as 120° , the free acid was recovered from the mass after treatment with water, thus showing that the two hydroxyl groups in the resorcinol residue could not have been displaced by chlorine.

Preparation of Paramethylsulphonfluoresceïn, $C_{20}H_{16}O_7S$.—A quantity of paramethyldioxybenzoylbenzenesulphonic acid is placed in a test-tube and the tube is immersed in a sulphuric-acid bath, which is gradually heated to a temperature of 170° . As the temperature of the bath rises the contents of the tube are occasionally stirred with a thermometer. The acid melts at about 130° to a deep-red liquid, and water-globules condense on the upper and colder part of the tube. After heating about an hour at 170° the material in the tube, which is light brown in color, becomes perfectly solid, and if the tube is now removed from the bath and plunged into cold water the material loosens from the sides of the tube and can be removed without difficulty. The products of the reaction are filtered with the aid of a pump and thoroughly washed. The paramethylsulphonfluoresceïn, thus freed to a great extent from impurities, is dissolved in caustic potash, in which it forms a solution of a surprising yellow-green fluorescence. The compound is then precipitated with sulphuric acid, and washed on a filter until the washings give no cloud with barium chloride. The process of washing is an extremely tedious one, requiring the greater part of three days to wash as much as was obtained in this experiment (about 0.600 gram); so that in all subsequent experiments the washing was done in a cylinder by decantation. While this material, as well as most of that which was subsequently obtained, was of a light brown color, products were sometimes obtained of a dark red material of the same chemical composition and, as far as could be determined, possessing the same properties as the lighter material. The analysis of the compound gave the following results :

0.0780 gram hydrous compound gave 0.0037 gram H_2O .

0.0940 gram hydrous compound gave 0.0043 gram H_2O .

0.2261 gram anhydrous compound gave 0.1360 gram BaSO_4 .

0.2411 gram anhydrous compound gave 0.1521 gram BaSO_4 .

0.1380 gram anhydrous compound gave 0.0519 gram H_2O and 0.3190 gram CO_2 .

0.0914 gram anhydrous compound gave 0.0309 gram H_2O and 0.2125 gram CO_2 .

	Calculated for $\text{C}_{20}\text{H}_{14}\text{O}_6\text{S}+\text{H}_2\text{O}$.	I.	II.	Found. III.	IV.	V.	VI.
H_2O	4.50	4.74	4.57
S	8.39	8.26	8.67
C	62.81	63.04	63.39
H	3.67	4.18	3.76

The water with which the material was first washed was treated with barium carbonate and partly decolorized with animal charcoal. The liquid was slightly fluorescent, but good crystals were deposited on cooling the concentrated solution, which gave the following analytical results :

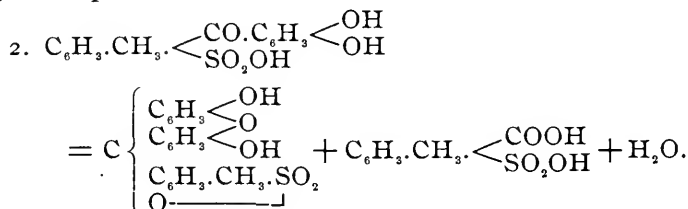
A specimen heated to 160° lost no weight.

0.1663 gram of the salt gave 0.1084 gram BaSO_4 .

0.0850 gram of the salt gave 0.563 gram BaSO_4 .

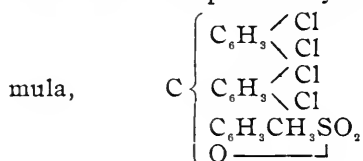
	Calculated for $\text{C}_6\text{H}_3(\text{CH}_3)\text{SO}_3\text{Ba}$.	Found. I.	II.
Ba	39.03	39.04	38.96

These analyses show that the reaction giving rise to the formation of paramethylsulphonfluorescein is to be represented by this equation :



Treatment of Paramethylsulphonfluorescein with Phosphorus Pentachloride.—Molecular quantities of these two substances were heated in a sulphuric-acid bath to 140° , and as the reaction proceeded small portions of phosphorus pentachloride were

added. When the evolution of gases had ceased the flask containing the products of the reaction was cooled and the material washed with water. This reddish-brown substance was found by a microscopic examination to consist of tolerably well-crystallized red grains. These crystals were soluble in alkali, with a dark-blue color and without fluorescence. Analysis of the compound corresponded to the composition of the fluorescein in which four chlorine atoms are introduced, and which in all probability should be represented by the for-



0.6225 gram crystallized compound gave 0.0839 gram H_2O .

0.2215 gram anhydrous compound gave 0.4020 gram CO_2 and 0.0598 gram H_2O .

0.1687 gram anhydrous compound gave 0.0829 gram BaSO_4 .

0.1011 gram anhydrous compound gave 0.0478 gram BaSO_4 .

0.1160 gram anhydrous compound gave 0.1360 gram AgCl.

	Calculated.	I.	II.	Found. III.	IV.	V.
4H ₂ O	13.19	13.48
C	50.64	50.00
H	2.54	3.00
S	6.76	6.79	6.48
Cl	29.94	29.01

Treatment of Paramethylsulphonfluorescein with Bromine.—

According to the directions given by Von Baeyer for the preparation of eosin, this compound was suspended in 4 times its weight of glacial acetic acid, and a 20-per cent. solution of bromine in glacial acetic acid added until enough bromine had been used to form a tetra-bromine substitution-product (8 equivalents). The mass was filtered, washed with glacial acetic acid, and then thoroughly washed with water. As this product was found to contain only a trace of bromine, perhaps mechanically held, the experiment was repeated in a flask so that the materials could be shaken together. Twice the necessary amount of bromine was added, and the mixture,

after having been shaken at intervals during an hour, was allowed to stand over night. It was washed with glacial acetic acid, which was driven off by continued heating on a water-bath, the washing with water having been omitted to avoid loss on account of the slight solubility of the material. The compound in alkaline solution has a beautiful eosin fluorescence, and was found on analysis to be an impure dibrom-paramethylsulphonfluoresceïn.

0.1969 gram hydrous compound gave 0.0114 gram H_2O .

0.1918 gram hydrous compound gave 0.2878 gram CO_2 and 0.0547 gram H_2O .

0.1633 gram hydrous compound gave 0.0693 gram $BaSO_4$.

0.1843 gram hydrous compound gave 0.0736 gram $BaSO_4$.

0.1845 gram hydrous compound gave 0.1201 gram $AgBr$.

	Calculated for $C_{20}H_{12}SO_6Br_2 \cdot 2H_2O$.	I.	II.	Found. III.	IV.	V.
H_2O	6.25	5.80
C	41.68	40.93
H	2.79	3.17
S	5.56	5.32	5.52
Br	27.76	27.92

Treatment of Orthosulphoparatoluic Acid with Larger Proportions of Resorcinol.—When the acid and resorcinol, in the proportion of 1 molecule of the former to 2 molecules of the latter, are allowed to act on each other, a sulphonphthaleïn is formed which contains four resorcinol residues; and, moreover, when such proportions of the acid and the phenol are employed as should be theoretically required for the formation of this sulphonphthaleïn with four resorcinol residues, there is then formed a sulphonphthaleïn containing six resorcinol residues. This last result is also reached when any excess of the phenol is used over that theoretically required to form the product containing four resorcinol residues. These statements are based on the results of three experiments which are described below. While the analytical results are not good, they are quite as near the theoretical numbers as could be expected in the case of compounds of their physical character. The materials obtained and used for analysis were dark amorphous powders, which in some cases were soluble in water to such an extent as to render their purification from more soluble im-

purities by continued washing impossible. They could not be heated with water because there was always present a substance whose melting-point is very low, and which served at slightly elevated temperatures to cause the entire mass of material to form a viscous liquid. However, in view of the fact that both of these substances possess the remarkable fluorescence which characterizes compounds that belong to the class of phthaleïns, together with the analyses obtained, we can see no objection to regarding them as complex sulphonphthaleïns.

Experiment 1.—Two and a half parts of orthosulphoparatoiuic acid and two parts of resorcinol (1 equivalent of the acid and 2 of resorcinol) were placed in a test-tube and heated by means of a sulphuric-acid bath at 160° until the dark-red liquid first formed had solidified, a process which requires about eight hours. From time to time the contents of the tube were stirred with a thermometer, which was kept in the tube during the entire operation.

There was a plentiful evolution of bubbles of water-vapor until near the end of the reaction, when the materials turned jet black and solidified. The products of the reaction were removed from the tube and washed thoroughly with water. The material on the filter was then dissolved in moderately concentrated caustic potash, precipitated from the alkaline solution with sulphuric acid, and washed on a filter until the wash-water showed no cloud when treated with barium chloride. The sulphonphthaleïn thus obtained is a light-brown powder when dry, and shows a beautiful green-red fluorescence in very dilute alkaline solution. The analysis of the sulphonphthaleïn gave the following results:

0.2147 gram hydrous compound gave 0.0197 gram H_2O .

0.2333 gram hydrous compound gave 0.0211 gram H_2O .

0.2734 gram hydrous compound gave 0.1243 gram H_2O and 0.6151 gram CO_2 .

0.2112 gram hydrous compound gave 0.1141 gram H_2O and 0.4740 gram CO_2 .

0.1822 gram hydrous compound gave 0.0672 gram $BaSO_4$.

0.1314 gram hydrous compound gave 0.0513 gram $BaSO_4$.

	Calculated for $C_{32}H_{22}O_8S_3H_2O$.	I.	II.	Found.		V.	VI.
				III.	IV.		
$3H_2O$	8.66	9.18	9.04
H	4.53	5.05	6.00
C	61.92	61.35	61.20
S	5.17	5.07	5.36

Experiment 2.—The method of procedure was the same as in Experiment I, except that 4 equivalents of resorcinol and 1 of the acid were used. The products of the reaction would not completely solidify, although the heating was carried on during two periods of eight hours each, and the material was much more difficult to handle, owing to the presence of a tar-like substance. Analytical results:

0.2721 gram hydrous compound gave 0.0224 gram H_2O .

0.2004 gram hydrous compound gave 0.0167 gram H_2O .

0.1821 gram hydrous compound gave 0.0829 gram H_2O and 0.4303 gram CO_2 .

0.1322 gram hydrous compound gave 0.0585 gram H_2O and 0.3091 gram CO_2 .

0.1570 gram hydrous compound gave 0.0467 gram $BaSO_4$.

0.1540 gram hydrous compound gave 0.0453 gram $BaSO_4$.

	Calculated for $C_{44}H_{30}O_{10}S_4H_2O$.	I.	II.	Found.		V.	VI.
				III.	IV.		
$4H_2O$	8.88	8.23	8.33
C	64.21	64.45	63.77
H	4.63	5.05	4.92
S	3.90	4.09	4.04

Experiment 3.—In this experiment 6 equivalents of resorcinol and 1 equivalent of the acid were used. During the heating the evolution of water-vapor was at times so violent that it was feared the material in the tube would be raised to the top. The product obtained in this reaction was much more troublesome than that obtained in either of the two experiments described. After the tube had cooled the contents were powdered in an agate mortar, but as soon as wash-water was applied the material formed a gelatinous mass which could only be imperfectly washed. The analyses of the product obtained gave the following results:

0.2572 gram hydrous compound gave 0.0209 gram H_2O .

0.3201 gram hydrous compound gave 0.0263 gram H_2O .

0.2211 gram hydrous compound gave 0.1053 gram H_2O and 0.5139 gram CO_2 .

0.1818 gram hydrous compound gave 0.0479 gram BaSO_4 .

0.1249 gram hydrous compound gave 0.0303 gram BaSO_4 .

0.3526 gram anhydrous compound gave 0.1395 gram H_2O and 0.9024 gram CO_2 .

	Calculated for $\text{C}_{44}\text{H}_{30}\text{O}_{10}\text{S}_4\text{H}_2\text{O}$.	I.	II.	Found. III.	IV.	V.	Calculated for VI. $\text{C}_{44}\text{H}_{30}\text{O}_{10}\text{S}_4$.	
$4\text{H}_2\text{O}$	8.88	8.13	8.22
C	64.21	63.38	69.79	70.39
H	4.63	5.29	4.39	4.01
S	3.90	3.63	3.33	...	4.28

Owing to a lack of time no attempts were made to obtain derivatives of these compounds. Although the sulphonphthaleïns as a rule are not compounds that can easily be obtained in pure condition, yet it is not at all impossible that these complex bodies may yield derivatives which will admit of more accurate analytical results than are here given.

Summary.

The results which have been reached in the course of the work described are in brief these:

1. When acid ammonium orthosulphoparatoluic acid is heated with resorcinol, the ammonium salt of paramethyldioxybenzoylbenzenesulphonic acid is formed.

2. The acid itself can be obtained by treating the ammonium salt with lead oxide and subsequently precipitating the lead with hydrogen sulphide.

3. The phenol-hydroxyl groups of the acid could not be replaced by residues of other acids.

4. The heating of the acid causes the formation of paramethylsulphonfluoresceïn.

5. All four hydroxyl groups of hydrous paramethylsulphonfluoresceïn can be replaced by chlorine.

6. The product obtained by treating paramethylsulphonfluoresceïn with an excess of bromine is a dibromine substitution-product which possesses the characteristic fluorescence of eosin in dilute alkaline solution.

7. Two other sulphonphthaleïns can be derived from orthosulphoparatoluic acid by treating it with resorcinol; one containing 4 and the other 6 resorcinol residues.

A STUDY OF THE CHEMICAL BEHAVIOR OF AMMONIA TOWARD FERRIC CHLORIDE AND FERROUS CHLORIDE¹.

BY ALFRED S. MILLER.

I. Conduct of Ammonia towards Ferric Chloride.

According to Rogstadius:²

1. Dry ammonia gas is not absorbed by ferric chloride at ordinary temperatures.
2. The action of ammonia gas is first a reduction of the ferric chloride to ferrous chloride.

According to H. Rose :³

1. The ferric chloride absorbs dry ammonia gas *without alteration of the external appearance*.
2. The formula for the compound is $\text{Fe}_2\text{Cl}_6 \cdot 2\text{NH}_3$.
3. The compound deliquesces in the air.
4. When thrown into water in considerable quantities, it dissolves with a hissing noise.

These statements are not sustained by the experiments which are given here.

The ferric chloride was made by heating, in a combustion tube, iron wire in a stream of dry chlorine gas. The ferric chloride was deposited, in the cool part of the tube, in dark green crystalline scales. These scales were sublimed in a stream of dry chlorine gas, and cooled in the same gas ; after which the free chlorine was swept out by dry air. The tube was then broken beyond the place where the wire had been placed, to prevent any carbon or other residue of the wire from mixing with the ferric chloride while removing the latter from the tube. On account of the extremely deliquescent nature of the ferric chloride, it is difficult to transfer it from one container to another without absorbing moisture.

Analysis:

¹ Extract from a thesis presented to the Faculty of the Post-graduate Department of Heidelberg University (Ohio), for the degree of Doctor of Philosophy.

² J. prakt. Chem., 86, 307.

³ Ann. der phys. Pogg., 24, 302.

	Per cent. obtained.	Calculated.
Cl	65.49	65.51
Fe	34.51	34.49
	<hr/>	<hr/>
	100.00	100.00

A rapid stream of dry ammonia gas was passed over this ferric chloride at 20° C. The action was immediate and so violent that in a short time it raised the temperature of about 200 cc. of water, in which the U tube with the ferric chloride had been placed, to 28° C., formed a melted mass through which a white powder was distributed, and a yellow powder was deposited in the cooler part of the tube. The temperature was reduced by changing the water, but, after passing the ammonia for half an hour, the tube burst, either from the heat or pressure produced by the action of the ammonia on the ferric chloride. The white powder was, no doubt, ammonium chloride, and the yellow powder, ammonium chloride colored with iron.

The ammonia was obtained by heating strong aqueous ammonia. The drying apparatus consisted of an empty Woulff bottle surrounded by water to condense any steam that might be carried over, another Woulff bottle filled with small pieces of charcoal, two cylinders filled with sticks of potash, and two tubes filled with lime. A guard tube filled with lime was used to prevent any moisture from coming in from the end of the apparatus.

Ammonia was again passed (more slowly at first) over ferric chloride for two hours, at 18° to 22.5° C. The color of the substance changed slowly to a reddish brown, the change of color being accompanied by a slight evolution of heat. Dry air was passed over this substance, at the end of the experiment, to take out free ammonia.

In analyzing this substance, separate samples were taken to determine the iron, chlorine, and ammonia. In my calculations in these experiments, I have expressed the composition of ferric chloride by the formula FeCl_3 . Those who prefer to write it Fe_2Cl_6 can easily make the change.

The iron was determined as ferric oxide, the chlorine as silver chloride, and the ammonia was determined volumetrically.

Fe.	Per cent. obtained. Cl.	NH ₃ .		Calculated for FeCl ₃ .2NH ₃ .
27.87	56.63	17.54	Fe	28.50
28.50	53.20	16.36	Cl	54.15
29.16	58.06		NH ₃	17.35
27.67	57.87			<hr/>
29.65	55.96			100.00
29.93				

These variations indicated that the substance was not homogeneous. Ammonia was passed, about the same length of time, over another sample of ferric chloride with similar results. This substance is less deliquescent than pure ferric chloride, and gave no reaction with potassium ferricyanide.

Ammonia was passed over ferric chloride for a longer time, with the following results:

Passed ammonia over ferric chloride

	Per cent. obtained.		
2½ hours...	{ Fe 27.45 Cl 52.24 NH ₃ 19.93	9 hours ..	{ Fe 21.96 Cl 42.77 NH ₃ 35.26
6 hours....	{ Fe 22.89 Cl 43.04 NH ₃ 32.26	10 hours ..	{ Fe 21.93 Cl 42.15 NH ₃ 35.44
7 hours....	{ Fe 22.31 Cl 43.27 NH ₃ 34.86	12 hours ..	{ Fe 20.00 Cl 38.50

Most of the substance had changed to a red powder and had a strong odor of ammonia. It was evident that some of the ammonia was held either very loosely chemically, or simply by absorption.

Through the manipulation of the substance for so many experiments and determinations, it possibly absorbed a trace of moisture, which enabled it to absorb a little more ammonia than it could have retained if perfectly dry. Air was again passed over the substance and another analysis was made, which showed a loss of ammonia. This was repeated with a similar result. The question now was, how to determine how much of the ammonia was held merely by absorption and how much chemically. The fact that some of the ammonia was given off at ordinary temperatures does not however prove that it was not held chemically. By adding an excess of ammonia to

a solution of cupric sulphate and evaporating the solution, dark blue crystals of *ammonio-cupric sulphate*, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, are deposited. These crystals lose all of their ammonia when exposed to the air, and yet the ammonia is, no doubt, in chemical combination.

Ammonia was passed over ferric chloride for fourteen hours. Dry air was passed over a sample of this while it was slowly heated (to aid the escape of possible free ammonia) at 61°C . This sample no longer gave off any odor of ammonia, and on analysis gave approximately five molecules of ammonia, $\text{FeCl}_3 \cdot 5\text{NH}_3$.

Analysis for iron and chlorine :

	Per cent. obtained.
Fe	22.50
Cl	42.97

Ammonia was again passed over ferric chloride for fifteen hours, and dry air was passed over this substance.

	Per cent. obtained.	
22 hours....	{ Fe 22.42	
	{ Cl 42.22	
26 hours....	{ Fe 22.47	
	{ Cl 42.73	
		Calculated for $\text{FeCl}_3 \cdot 5\text{NH}_3$.
27½ hours...	{ Fe 22.56	22.62
	{ Cl 42.86	42.97
	{ NH_3 34.52	34.41
	<hr/>	<hr/>
	99.94	100.00

Approximately the same result was obtained by slightly heating the substance while passing dry air over it for $27\frac{1}{2}$ hours. The air was passed through a solution of potash, then through concentrated sulphuric acid and two tubes filled with lime. The usual guard tube was used, and the air was drawn through the apparatus by an aspirator.

This does not prove that more of the ammonia was not held chemically, but it seems to prove that ferric chloride will hold 5 molecules of ammonia at ordinary temperatures in a perfectly dry atmosphere.

A sample of this substance was placed in a U tube and dry air was passed over it, while the tube was heated to 100°C .

Analysis :

	Per cent. obtained.	Calculated for $\text{FeCl}_3 \cdot 4\text{NH}_3$.
Fe	24.30	24.29
Cl	46.16	46.14
NH_3	29.53	29.57
	<hr/> 99.99	<hr/> 100.00

Another sample was treated in the same way for five hours, and gave approximately the same result. The compound, therefore, became at 100°C. , $\text{FeCl}_3 \cdot 4\text{NH}_3$. A sample heated at 120°C. showed a loss of ammonia of nearly 2 per cent. more.

Another sample was treated in the same way and heated to 200°C. , in a paraffin-bath. A yellowish white deposit of ammonium chloride was deposited in the cooler part of the tube.

Analysis for iron and chlorine :

	Per cent. obtained.	Calculated for $\text{FeCl}_3 \cdot \text{NH}_3$.
Fe	30.28	31.21
Cl	56.95	59.29

Below 280°C. the substance was entirely dissociated, leaving a small residue of iron in the ferric condition.

A sample of the compound was placed in water for a week or longer. At the end of this time the substance had not passed into solution, and showed no apparent change. It was filtered off and washed. After being dissolved in nitric acid, it gave no reaction for ammonia nor for chlorine. Both the ammonia and the chlorine were found in the filtrate. Samples placed on a filter and washed with water gave the same results. The compound, when treated with water, evidently gives up its ammonia and its chlorine, and takes up the hydroxyl radicle without going through the processes of solution and reprecipitation.

In order to avoid all possibility of absorption of moisture by the ferric chloride while transferring it from the combustion-tube, in which it was made, to a U tube for the purpose of passing ammonia over it, a combustion-tube was bent, at one end, into a U tube. The ferric chloride was made in the combustion-tube as before, and volatilized in a stream of chlorine gas until it had collected in the U tube. Dry air was then passed through the tube for half an hour, to take out all free chlorine. The ammonia apparatus was then attached to

the tube. Ammonia was passed over this ferric chloride for twenty hours, at 18° to 20° C.

Analysis for iron and chlorine:

	Per cent. obtained.	Calculated for $\text{FeCl}_3 \cdot 6\text{NH}_3$.
Fe	21.01	21.16
Cl	40.17	40.20

No air was passed over this substance before removing it from the tube. The slight excess of 0.18 per cent. of ammonia over six molecules, $\text{FeCl}_3 \cdot 6\text{NH}_3$, which this analysis indicates, was probably due to free ammonia. The experiment indicates that 6 molecules of ammonia is the maximum saturation-capacity of ferric chloride.

A series of 3 U tubes was arranged, a sample of the substance was placed in each U tube, and dry air was passed through the U tubes, while the first was heated to 100° C., the second to 110° – 116° C., and the third to 150° – 159° C., for two hours.

Analysis of the third sample:

	Per cent. obtained.	Calculated for $2\text{FeCl}_3 \cdot 5\text{NH}_3$.
Fe	27.31	27.36
Cl	51.79	51.99

Analysis of the second sample:

	Per cent. obtained.	Calculated for $\text{FeCl}_3 \cdot 4\text{NH}_3$.
Fe	24.23	24.29
Cl	46.49	46.15

The third sample was again heated to 150° – 154° C., and dry air at ordinary temperature was passed over it.

Analysis:

	Per cent. obtained.
Fe	27.47
Cl	53.04

A fourth sample was heated to 170° C., for three hours. The first two hours air at ordinary temperature was passed over it, the third hour the air was passed through a tube heated to 100° C., before it reached the substance.

Analysis:

Fe	27.86
Cl	52.89

Above 100° C. the substance began slowly to dissociate.

The chlorine and the ammonia, which were driven off, formed ammonium chloride, part of which was deposited in the cool part of the tube and part in the substance where the temperature was reduced by a stream of air at lower temperature, or by reason of its being removed from the side of the tube to the interior, where the temperature was lower.

It will be noticed that when the third sample was heated to 150° – 159° C., and air was passed over it, which had passed through 2 tubes heated to 100° – 116° C., more of the ammonium chloride, which formed, was carried out of the substance. When the same sample was treated in the same way except that air was passed over it at ordinary temperature, more of the ammonium chloride collected in the substance, which explains the increase in the weight of chlorine. The weight of chlorine is high in the second sample, which is due to the formation of ammonium chloride.

The following results will show that the ferric chloride absorbs the ammonia very slowly :

Passed ammonia :

Absorbed.			Temperature.	
2	hours.....	17.54 per cent. NH_3	20° – 23°	C.
$2\frac{1}{2}$	"	19.93 " " "	20° – 22°	C.
6	"	32.26 " " "	19° – 20°	C.
7	"	34.86 " " "	18° – 22°	C.
10	"	35.44 " " "	18° – 20°	C.

The amount of ammonia does not depend entirely upon the time that the gas is passed over the ferric chloride, but is conditioned also by the temperature, and the rapidity and strength of the stream of the gas. Freshly made ferric chloride takes up the gas faster than that which is a week or so old.

When the ferric chloride has absorbed 6 molecules of ammonia, $\text{FeCl}_3 \cdot 6\text{NH}_3$, most of it consists of a red powder.

I have made more than fifty determinations in conducting these experiments. Many of these were made to discover what action had taken place in different stages of the experiments, and would hardly be of interest to the reader. At no stage of the experiments, either in working ammonia into the compound or in taking it out, did it give any reaction with potassium ferricyanide. Ammonia, therefore, does not

reduce ferric chloride as Rogstadius, who has investigated this subject, states.

When the ferric chloride has taken up 6 molecules of ammonia, the compound that is formed is not deliquescent, and is not soluble in water nor in any of the ordinary solvents. The mineral acids dissolve it to a red solution.

Summary.

1. Anhydrous ferric chloride will absorb 6 molecules of ammonia, $\text{FeCl}_3 \cdot 6\text{NH}_3$, or $\text{Fe}_2\text{Cl}_6 \cdot 12\text{NH}_3$, at ordinary temperatures.

2. It will retain 5 molecules of ammonia, $\text{FeCl}_3 \cdot 5\text{NH}_3$, in a perfectly dry atmosphere at ordinary temperatures.

3. It becomes $\text{FeCl}_3 \cdot 4\text{NH}_3$, at 100°C .

4. The ammonia compound does not dissolve in water: the mineral acids dissolve it to a red solution.

5. It is not deliquescent.

6. The chlorine and the ammonia can be washed out.

7. The compound showed a gradual dissociation, with formation of ammonium chloride, from 100°C . to 280°C .; just below 280°C . it was entirely dissociated.

8. The compound absorbs dry chlorine gas with the evolution of a considerable amount of heat.

II. Conduct of Ammonia towards Ferrous Chloride.

The following methods for making ferrous chloride were tried: 1. By heating iron wire in a stream of dry hydrochloric acid gas; 2. By heating finely divided iron mixed with 3 times its weight of ammonium chloride; 3. By heating finely divided iron mixed with charcoal, in a stream of dry hydrochloric acid gas; 4. By heating ferric chloride in a stream of dry hydrogen. The last of these methods gave the best results.

It was found that ferrous chloride will absorb approximately 6 molecules of ammonia at ordinary temperatures, and form a white powder, $\text{FeCl}_2 \cdot 6\text{NH}_3$. These results were also obtained by Rogstadius.¹

The compound turns brown when it is exposed to the air. It is difficult to keep it from oxidizing.

¹ J. prakt. Chem., 86, 310; Fehling: Handwörterbuch der Chemie, p. 1106.

A sample of the compound was placed *in vacuo* over sulphuric acid for sixteen hours.—

Analysis:

	Found.	Calculated for $\text{FeCl}_2 \cdot 5\text{NH}_3$.
Fe	26.01	26.40
Cl	32.51	34.44

Some of the iron was evidently oxidized.

A sample of the compound was put into a glass tube and hydrogen was passed over this sample for an hour, while the tube was heated to 100°C .

	Found.	Calculated for $\text{FeCl}_2 \cdot 2\text{NH}_3$.
Fe	34.65	34.78
Cl	43.81	44.05

Another sample was treated in the same way for three hours.

	Found.
Fe	35.08
Cl	44.26

This indicates that it approximates to the formula $\text{FeCl}_2 \cdot 2\text{NH}_3$, at 100°C .

Ammonia is more easily absorbed by ferrous chloride than by ferric chloride. The absorption of ammonia is accompanied by the evolution of a considerable amount of heat. A U tube containing ferrous chloride was placed in about 150 cc. of water, and ammonia was passed through the U tube. In twenty minutes the temperature of the water rose from 19° to 24°C .

I take this opportunity to express my gratitude to Dr. John M. Stillman, Professor of Chemistry in the Leland Stanford Junior University, who suggested the work to me, and in whose laboratory the work was done. His ready and willing counsel, and the kindly interest which he manifested in my work, contributed in a large measure to the success of these experiments.

Contribution from the Chemical Laboratory of Harvard College.

LXXXVII.—ACTION OF SODIC ALCOHOLATES ON CHLORANIL. ACETALS DERIVED FROM SUBSTITUTED QUINONES.¹

BY C. LORING JACKSON AND H. S. GRINDLEY.

INTRODUCTION.

During the study of the action of sodic alcoholates, sodium malonic ester, and similar reagents upon tribromdinitrobenzol and related substances,² carried on now for some years in this laboratory, it has been observed repeatedly that one of the atoms of bromine is replaced by hydrogen. In all this work, however, the bromine replaced by hydrogen has stood in the meta position to two other atoms of bromine, and, as it was possible that this strange reaction depended on the symmetrical position of the three atoms of bromine, we undertook the study of a substance with a different constitution; and for this purpose selected chloranil, in which no one of the atoms of halogen is in the meta position to two others. While this substance was well fitted for our work, because the atoms of chlorine which it contains can be replaced with comparative ease; on the other hand the action of most of these reagents with it had been already studied by Stieglitz,³ Ikuta,⁴ Kehrman,⁵ and others, and in no case could we find any mention of a direct replacement of chlorine by hydrogen; but still as it was possible that the compounds formed by such a replacement might have been overlooked among the secondary products of some of these reactions, or might be formed under other conditions, we have carried through our experiments. In fact, one of them has proved that, when sodic methyrate acts upon chloranil, a reduction takes place, but the hydrogen, instead of replacing chlorine, reduces part of the chloranil to the corresponding tetrachlorhydroquinone. The work with chloranil, therefore, did not throw light on the replace-

¹ The work described in this paper formed a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Science, by H. S. Grindley. It was presented to the American Academy of Arts and Sciences May, 1894.

² This Journal, **11**, 93, 541; **12**, 7, 164, 289; **13**, 164; **15**, 607.

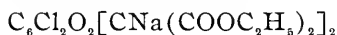
³ This Journal, **13**, 38.

⁴ Proc. Am. Acad., **26**, 295.

⁵ J. prakt. Chem., [2], **40**, 365.

ment of bromine by hydrogen in the tribromdinitrobenzol, because of the presence of the two atoms of quinone oxygen, which seized upon the hydrogen before it could replace the halogen. In the meantime, however, our experiments have led to interesting results of another sort, which are described in this paper.

The action of potassic phenylate on chloranil was the first selected for study, and we found that, if the substances were mixed in proportion of two molecules of the former to one of the latter, the product was dichlordiphenoxyquinone, $C_6Cl_2(OC_6H_5)_2O_2$, which melts at 243° , and gives a hydroquinone melting at 197° – 198° when treated with reducing agents. With the object of replacing the two remaining atoms of chlorine we next treated the dichlordiphenoxyquinone with aniline, but instead of acting on the atoms of chlorine this reagent attacked the phenoxy groups, giving dichlordianilidoquinone and phenol, behaving in this respect in the same way as dichlordimethoxyquinone which, Kehrman¹ found, was converted by treatment with aniline into dichlordianilidoquinone. This action we found was the normal one for our substance: for example, sodium malonic ester gave with the dichlordiphenoxyquinone the dichlorquinonedimalonic ester melting at 132° , discovered by Stieglitz;² and, strangely enough, this indirect method of preparing the substance gives a better yield than the direct action of sodium malonic ester on chloranil, for while Stieglitz by this latter method obtained only about 10 per cent., our yield was as high as 27 per cent. The beautiful bright blue sodium salt



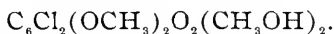
was obtained, and analyzed; it is stable for a malonic ester salt. The "deep pure violet color, resembling exactly a concentrated solution of potassium permanganate," obtained by Stieglitz, upon the addition of sodic hydrate to the substance, is due, according to our observations, to some decomposition of the salt brought about by an excess of the alkali. The solution of the pure salt has the full blue color of aniline-blue.

Sodic methylate acted on the dichlordiphenoxyquinone like

¹ J. prakt. Chem. [2], 40, 370.

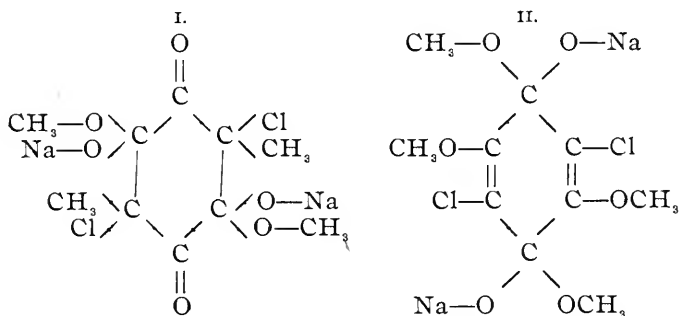
² This Journal, 13, 38.

the two reagents already mentioned : that is, the two phenoxy groups were replaced by two methoxy groups ; but this action was followed by another and more interesting one, which formed a crystalline salt, appearing as a precipitate if the amount of the methyl alcohol used as the solvent was small. Upon the addition of an acid to this salt a white substance was set free having the following formula :



The sodium salt was also analyzed, and proved to have the formula $\text{C}_6\text{Cl}_2(\text{OCH}_3)_2\text{O}_2(\text{CH}_3\text{ONa})_2(\text{CH}_3\text{OH})_2$. The two molecules of methyl alcohol appearing in this formula are evidently only alcohol of crystallization, as they could be easily driven off by heat. The corresponding ethyl and methylethyl compounds,

$\text{C}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2\text{O}_2(\text{C}_2\text{H}_5\text{OH})_2$ and $\text{C}_6\text{Cl}_2(\text{OCH}_3)_2\text{O}_2(\text{C}_2\text{H}_5\text{OH})_2$, were also obtained, and resembled the methyl compound most closely in properties. In considering the way in which the two molecules of methyl alcohol (or sodic methyrate) are attached to the molecule of $\text{C}_6\text{Cl}_2(\text{OCH}_3)_2\text{O}_2$, only two formulas seemed to us sufficiently probable to merit discussion. In the first of these (I.) the double bonds of the benzol ring are broken, and the radicles NaO and CH_3 added directly to the ring after the manner of the bromine and chlorine addition-compounds discovered by Nef.¹ In the second (II.) the NaO and CH_3 have been added to the two carbonyl groups of the quinone, transforming it into a substance closely related to the acetals.



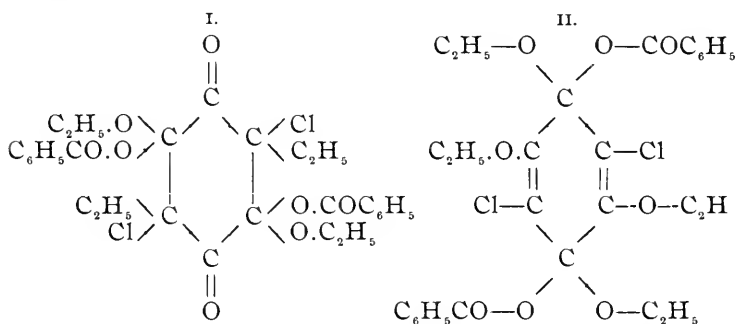
¹ This Journal, 12, 483 ; 13, 422.

The various isomeric forms of formula I. need not be considered, as the arguments which follow will apply as well to them as to this one. From the properties of this substance, it is not possible to decide between these formulas. It is white, like Nef's bromine addition-products, but an acetal like formula II., would also probably be white, as the colors of chloranil and its derivatives undoubtedly depend on the fact that they are quinones, and in such an acetal as this the quinone nature is obliterated. Its most striking property is the ease with which the free substance loses the two additional molecules of methyl alcohol, since it passes into dichlorodimethoxyquinone when heated to temperatures from 160° to 195° ; the same change is brought about by dilute sulphuric or hydrochloric acid, slowly in the cold, more rapidly when the mixture is warmed gently. While this instability is in harmony with the second formula given above, it is hard to connect it with the first, as it seems improbable that a methyl group attached directly to the benzol ring, as in formula I., could be so easily removed. It must be remembered in this connection, however, that Stieglitz,¹ by treating the dichloroquinonedimalonic ester with dilute sodic hydrate in the cold obtained parachlorhydroxyquinone, $C_6Cl(OH)H_2O_2$. As in this case carbon atoms attached to the quinone ring were removed by a dilute alkali in a few minutes, it might be that the methyl group in formula I. could be removed under the conditions observed by us. The objection to formula I., mentioned above, might also be met by substituting for it one in which the radicles added were Na and CH_3O instead of NaO and CH_3 as in that formula, but such an addition seems to us at the best improbable. It should be remarked here that Nef's bromine addition-compounds were decomposed with the utmost ease by alkalis, but were very stable in contact with acids, being crystallized from strong nitric acid; our substances show just the opposite behavior, as they are rather remarkably stable toward alkalis; but this difference might be due to the difference in the nature of the radicles added (Br_2 in one case, and NaO and CH_3 in the other) rather than to a difference in the structure of the compounds.

¹ This Journal, 13, 38.

Since, as explained above, the known properties of our new substance were not sufficient to prove the correctness of one or the other of the two formulas proposed, we next turned our attention to some experiments with derivatives of this substance, or rather of the corresponding ethyl compound, which have settled the question conclusively.

To obtain material for this work, which would be possessed of the requisite stability, we replaced the sodium in the salt of our substance with the benzoyl radicle, forming a compound which must have one of the following formulas, according as one or the other hypothesis about these substances is adopted :



In formula I. the carbonyl groups are unaffected, and the body should therefore retain the properties of a diketone. In formula II., on the other hand, the carbonyl groups having been transformed into acetal groups, the body should have lost its diketone nature. Accordingly, a substance constituted like formula I. should be converted by reducing agents into a substance containing secondary hydroxyl groups, and by the chloride of hydroxylamine into a mon- or dioxime. Upon treating our substance with zinc-dust and glacial acetic acid, (which we have found the most efficient agent for converting quinones into hydroquinones,) it remained entirely unaltered, and the same result was obtained when we tried to act on it with chloride of hydroxylamine. The substance therefore shows neither of these characteristic reactions of the diketones and must be constituted according to formula II. To meet the not overstrong objection that the diketone prop-

erties of the substance might have been weakened or destroyed by the presence of radicles attached to the ring, we treated dichlordiethoxyquinone with the reducing mixture, and also with chloride of hydroxylamine, and in both cases obtained a satisfactory quinone reaction. We tried also to determine the constitution of our substance in another way. This consisted in making the dichlordiethoxyquinone tetraethylacetal $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$ by replacing the sodium in the sodium salt $C_6Cl_2(OC_2H_5)_2(ONa)_2(OC_2H_5)_2$ by ethyl, and then treating this dissolved in chloroform with bromine in the hope of making an addition-product similar to those of Nef. The result of this experiment was negative, as no bromine was taken up, but this cannot be accepted as an argument against formula II., since Nef¹ found that dichlordiethoxyquinone itself gives no addition-product with bromine,—a result which we can confirm. The failure of the tetraethylacetal to form addition-compounds must be ascribed, therefore, to the presence of the two atoms of chlorine and two ethoxy groups attached to the quinone ring, rather than to the absence of double bonds.

It is perhaps worth noting that the formation of these hemiacetals is easily explained by the diketone formula of quinone, but cannot be brought into harmony with the peroxide formula, so far as we can find. Our work, therefore, would have been of value in determining the constitution of quinone if it had been done before this question was finally settled by Nef's proof of the diketone constitution through his work on the action of bromine on argentic chloranilate.²

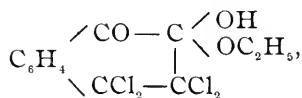
Since, as we have just proved, our new substance has the two molecules of methyl alcohol attached to the two carbonyl groups of the dichlordimethoxyquinone, it belongs to the class of acetals, and we propose to call it and similarly constituted bodies hemiacetals, because only half of the hydrogen in the hypothetical mother-group of the acetals, $=C=(OH)_2$, has been replaced by the organic radicle. Such hemiacetals are not especially uncommon, the most familiar examples being the alcoholates of ordinary chloral and of butylchloral. Jacobsen,³

¹ This Journal, **11**, 20, 24.

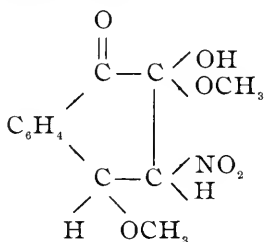
² *Ibid.* **12**, 466.

³ Ber. d. chem. Ges., **4**, 215.

and later Renard,¹ claimed that they obtained the corresponding compound of acetaldehyde, $\text{CH}_3\text{CH}(\text{OH})(\text{OC}_2\text{H}_5)$, but do not agree in regard to its boiling-point, and apparently assign to it a much greater stability than would be expected in such a substance. Without multiplying examples, we pass at once to some compounds more nearly related to ours, recently obtained by Zincke with some of his scholars. Zincke and Arnst,² by the action of alcohol on tetrachlordiketohydro-naphthalin have obtained a compound,



which is tolerably stable in the cold, but decomposes by heat, like our hemiacetal. The corresponding para compound formed no such derivative. Zincke and Neumann,³ by the action of alcohol on nitro- β -naphthoquinone, obtained a substance the formula of which was made out as follows :



Still later, Zincke and Schaum⁴ have made similar compounds from the isomeric heptachlorketotetrahydrobenzols by the action of sodic methylate. Although Zincke's work shows that ring-ketones, orthodiketones, and orthoquinones are capable of forming such hemiacetals ; so far as we can find, our compound is the first of this class to be made from a paraquinone, and the compound of Zincke's which approaches most nearly to it, the orthoquinone derivative, differs from it strikingly, for, whereas in our compound both carbonyls are converted into hemiacetal groups, in Zincke and Neumann's only one of the carbonyl groups is thus affected, and at the

¹ Ber. d. chem. Ges., 8, 132.

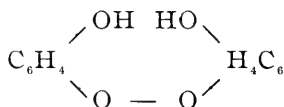
³ *Ibid.* 278, 173.

² Ann. Chem. (Liebig), 267, 319.

⁴ Ber. d. chem. Ges., 27, 537.

same time a molecule of sodic methylate is added to the ring by the breaking of a double bond. It should be mentioned here that J. U. Nef¹ has assumed the formation of addition-products of water or hydrochloric acid with the carbonyls of quinone in explaining the formation of hydroquinone by the action of water,² or substituted hydroquinones by the action of hydrochloric acid on quinone;³ but he supposes that these intermediate products break up immediately, and none of them have been isolated.

The discovery of the hemiacetals of the quinones has suggested to us a possible explanation of the constitution of quinhydrone and the bodies related to it. The most important of these substances are quinhydrone formed from one molecule of quinone and one of hydroquinone; resorcinquinone, from one molecule of quinone and one of resorcin; phenoquinone, from one molecule of quinone and two of phenol; and quinhydronedimethyl ether, from one molecule of quinone and two of the monomethyl ether of hydroquinone. The state of our knowledge of the constitution of these substances is described in the following quotation from a paper on this subject by Nietzki:¹ "Aus vorstehenden Versuchen scheint hervorzugehen, dass das Chinhydron, das Chinouresorcin, blosse Additionsproducte des Chinons mit phenolartigen Körpern sind, und zwar scheint hierbei die Zahl der in letzteren enthaltenen freien Hydroxyle stets den beiden Chinonsauerstoffen zu entsprechen. Eine Formel im Sinne der Structurtheorie lässt sich für diese Körper wohl augenblicklich kaum aufstellen, denn die von Kekulé für das Chinhydron vorgeschlagene Structurformel



lässt sich für die Verbindungen des Chinons mit einwerthigen Phenolen nicht mehr anwenden. Aus dem von O. Hesse

¹ This Journal, **13**, 427; Ann. Chem. (Liebig), **270**, 323; Clark: This Journal

14, 553.

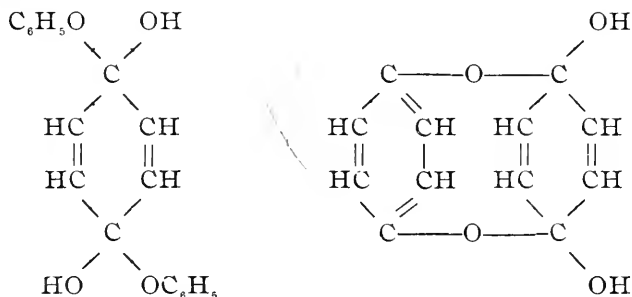
² Hesse: Ann. Chem. (Liebig), **220**, 367; Ciamician: Gazz. chim. Ital., **16**, 111.

³ Levy; Schultz: Ann. Chem. (Liebig), **210**, 133; Sarauw: *Ibid.* **209**, 93.

⁴ *Ibid.*, **215**, 136.

beobachteten Verhalten des Chinhydrons gegen Essigsäureanhydrid scheint jedoch hervorzugehen dass das Chinhydron keine freien Hydroxyle enthält. Auch das von Wichelhaus beobachtete Verhalten des Monomethylhydrochinons spricht dafür, dass Substitutionsproducte des Chinhydrons in den Hydroxylgruppen nicht existiren."

It appears from this quotation that there is no satisfactory theory for the constitution of these compounds, since the statement that they are addition-products amounts to saying that we have no theory on the subject. We would, therefore, advance the following theory in regard to the constitution of these bodies: that they are hemiacetals similar to those described in this paper; in phenoquinone the phenol, in quinhydrone the hydroquinone, taking the place of the methyl or ethyl alcohol, which is added to the substituted quinones in our new substances. On this theory the graphical formulas of phenoquinone and quinhydrone would be written as follows:



The principal arguments in favor of this theory are the following: It requires the union of one molecule of quinone with one molecule of a diatomic phenol such as hydroquinone or resorcin, but with two of a monatomic phenol like common phenol or monomethylhydroquinone, and is in this respect in accordance with the facts. Such substances would not be formed when the hydroxyl groups of the phenols had been converted into alkyloxyl groups, and dimethylhydroquinone has no action on quinone. The products should be unstable, as we have found that the stability of our new hemiacetals depends on the number and strength of the negative radicles at-

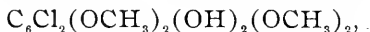
tached to the quinone ring, and, in these cases, where there are no negative radicles, we should expect a very slight stability. As a matter of fact, these substances are not only decomposed by acids or alkalies, but quinhydrone even by solution in neutral solvents.¹ The action of acetic anhydride giving diacetylhydroquinone and quinone,² which is brought up by Nietzki as a proof of the absence of free hydroxyl, is really in accordance with our theory, as our dimethylhemiacetal with acetic anhydride gave methyl acetate and the quinone from which the hemiacetal was derived. All these observed facts, therefore, are in harmony with our theory. Against it is the marked color of all this quinhydrone group, whereas our hemiacetals are colorless. This may be due, however, to the difference in the nature of the radicles attached to the carbonyl groups, our hemiacetals containing methyl or ethyl, the quinhydrone group aromatic radicles, which might well give more colored compounds. It may be remarked in this connection, that, while the methyl or ethyl ether of resorcin is colorless, the simple resorcin ether itself is reddish brown. An attempt will be made next year to find other parallel cases. Another objection to our theory is, that no salts have been obtained from phenoquinone, whereas the substance, according to our formula, contains two free hydroxyls. Wichelhaus, who states that he obtained no salts of it, adds that the substance turns blue when treated with alkalies; this may indicate the formation of a salt not yet isolated. We have attempted to test our theory by experiment in this direction, but so far with little result. By treating phenoquinone with sodic ethylate, not in excess, we obtained a green salt; but, as much phenol was found in the filtrate, we are inclined to consider this salt at present rather a product of the action of sodic ethylate on the quinone formed by the decomposition, than a salt of the phenoquinone itself. If this interpretation of the observation is true, it has no bearing on our theory, as it shows only that the phenoquinone is easily decomposed by alkalies, this decomposition taking place before it had time to form a salt. We then tried the action of sodic phenylate on

¹ Clark : This Journal, **14**, 574.

² Hesse : Ann. Chem. (Liebig), **200**, 248.

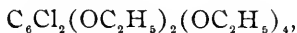
quinone, as according to our theory this should act as well, or even better than free phenol, and we have succeeded in getting an action in this case, a strongly colored product being formed; but these experiments were undertaken so late in the year that we had no time to isolate this substance for study. We should add that in the action of potassic phenylate on chloranil, described at the beginning of the experimental part of this paper, there are strong indications of the formation of a diphenyl-hemiacetal, as the liquid took on a blue-black color in the cold, which upon heating changed to the red of the dichlordiphenoxyquinone. The isolation of this hemiacetal, if possible, will throw a great deal of light upon our theory of the nature of phenoquinone. All these lines of work will be taken up in this laboratory during the next academic year, and we hope that by means of these experiments we shall succeed in testing thoroughly our theory that quinhydrone and phenoquinone are hemiacetals of quinone. The curious addition-compounds of the nitranilines and quinones¹ will also be considered in this connection.

The dichlordimethoxyquinone dimethylhemiacetal



although most conveniently made from the dichlordiphenoxyquinone by the action of sodic methylate, can also be obtained by the action of the same reagent on dichlordimethoxyquinone, or even on chloranil. In this last case the first product is a green sodium salt, which by treatment with water yields the sodium salt of the hemiacetal and the tetrachlorhydroquinone, mentioned at the beginning of this paper. With sodic ethylate and chloranil we have not succeeded in obtaining the corresponding ethyl compound; it may be, however, that this result was due to not finding the proper conditions for the reaction.

The dichlordiethoxyquinone tetraethylacetal



alluded to in the discussion of the constitution of the hemiacetals, was made by the action of ethyl iodide in the cold on the silver salt of the corresponding hemiacetal. The yield was

¹ Hebebrand: Ber. d. chem. Ges., **15**, 1973; Niemayer: Ann. Chem. (Liebig), **228**, 332.

exceedingly small, most of the hemiacetal dropping back to dichlorodiethoxyquinone. Its properties were strangely unlike those of the corresponding hemiacetal, for whereas the dichlorodiethoxyquinone hemiacetal was essentially insoluble in all solvents, the tetraethylacetal was so easily soluble in all the common solvents except water, that it was hard to crystallize it from any of them. The most striking property of the hemiacetal was its instability, since it gave up ethyl alcohol at temperatures from 140° to 143° , becoming converted into the dichlorodiethoxyquinone (melting at 104° – 105°); the tetraethylacetal, on the other hand, melts without decomposition at 101° – 102° , and from 205° to 275° sublimes apparently unaltered. The hemiacetal is converted into dichlorodiethoxyquinone when treated with acids, even more easily than by heat, dilute sulphuric or hydrochloric acid acting on it slowly even in the cold, rapidly when warmed. This is its most marked property; in fact, it is so susceptible to the action of acids that in our earlier preparations we obtained a considerable amount of dichlorodiethoxyquinone by drying the hemiacetal at ordinary temperatures, when it had not been washed enough to remove the last traces of acid. In order to bring about a similar decomposition of the tetraethylacetal it is necessary to boil it with sulphuric acid of specific gravity 1.44. A more dilute acid does not act upon it, and even this rather strong sulphuric acid has no action in the cold. With alkalis the hemiacetal forms crystalline salts, which are comparatively stable, since they dissolve in water without decomposition, and can be kept in the dry state for a moderate length of time. The stability of the substance toward alkalis is in marked contrast to its behavior with acids, as it is necessary actually to boil it with sodic hydrate in order to convert it into chloranilic acid. The tetraethylacetal can of course form no salts, as it contains no hydroxyl. It is even more stable toward alkalis than the hemiacetal, as sodic hydrate even when boiling or mixed with alcohol does not decompose it. Finally the hemiacetal is amorphous, the acetal crystallizes finely, so that almost the only property which they have in common is their white color. The salts of the hemiacetals which are not derived from the alkalis are insoluble in water.

The dichlordiethoxyquinone dibenzoyldiethylacetal,



also mentioned in the discussion of the constitution of the hemiacetals, was made by the action of benzoyl chloride on the sodium salt of the corresponding hemiacetal suspended in alcohol. In this case the yield is good, about 66 per cent. of the theoretical, so that this substance is much more accessible than the tetraethylacetal; it crystallizes well, and melts at 170° . It is a curious fact that none of the benzoyl compound is formed, if the sodium or silver salt of the hemiacetal is suspended in ether instead of alcohol, and treated with benzoyl chloride. In order to obtain this benzoyl compound, therefore, it is essential to use alcohol as the diluent. The reaction with ether is apparently the same as that which occurs when the free hemiacetal or its sodium salt is heated to 100° with benzoyl chloride, the products in this case being dichlordiethoxyquinone and ethyl benzoate.

When the dichlordiethoxyquinone dibenzoyldiethylacetal is heated with sulphuric acid of specific gravity 1.44, it is converted into a new substance, the analysis¹ of which gave numbers corresponding to the formula $\text{C}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2(\text{OCOC}_6\text{H}_5)_2\text{O}$. This body must be formed by the saponification of two ethoxy groups by the sulphuric acid, whereas we should have expected that the acid would have attacked rather the two benzoate groups. Our experiments have not as yet given us any means of determining which pair of ethoxy groups has been saponified. From the formula established by analysis we should infer that, after the two ethoxy groups had been converted by saponification into two hydroxyls, a molecule of water was eliminated, leaving the atom of oxygen spanning the benzol ring between two atoms of carbon in the para position to

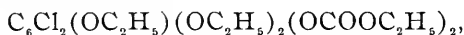
¹ As our first analytical results approached the numbers calculated for the dichlordiethoxyhydroquinone dibenzoate, $\text{C}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2(\text{OCOC}_6\text{H}_5)_2$, we thought that perhaps we had in hand this substance mixed with an obstinately adhering impurity, and accordingly we made it from the substituted hydroquinone in order to compare it with our substance, but found that the two were not identical, since it melts at 215° , while the melting-point of our new substance is 142° . The bad results from our first analyses we found afterward to be due to the difficulty in securing a complete combustion of our saponification-product, and, after taking special precautions to insure this, numbers were obtained from very carefully purified preparations agreeing excellently with those for the formula given above.

each other. Our substance, therefore, would have some analogy to cineol, if the constitution ascribed to it by Brühl² is correct. We realize fully, however, that such an unusual constitution as this should not be considered established without the most convincing proof, and, as at present we are unable to give this, we propose it only as that which accords best with the results of analysis and the method of preparation of the substance. We have made some attempts to prepare derivatives of this substance in order to throw light on its constitution, and have found that hydriodic acid converts it into a substance probably having the formula



and melting at 164° , but we have not yet studied this substance thoroughly enough to advance any theory in regard to its constitution. Aniline also forms one or more compounds with the saponification-product, which we have not yet succeeded in bringing into a state fit for analysis. We must content ourselves, therefore, at present with this preliminary statement of our experiments on this subject, the study of which will be continued in this laboratory during the next academic year.

The methyl compounds $\text{C}_6\text{Cl}_2(\text{OCH}_3)_2(\text{OCOC}_6\text{H}_5)_2$, melting at 193° , and $\text{C}_6\text{Cl}_2(\text{OCH}_3)_2(\text{OCOC}_6\text{H}_5)_2\text{O}$, melting at 205° – 206° , which agree with the corresponding ethyl compounds in every respect, have also been prepared. In order to determine whether other acid radicles would act like benzoyl, we treated the sodium salt of the diethyl hemiacetal with chloro-carbonic ester, and obtained the dichlorodiethoxyquinone diethylacetaldicarbonic ester



which melts at 122° – 123° . In view of our experiments with the benzoyl derivative, the saponification of this substance promises interesting results.

We have tried a number of experiments to determine the limits of the formation of hemiacetals from quinones; and have found that the dibromdiphenoxyquinone (melting-point 266° – 267°) made from bromanil, forms a hemiacetal, which seems to be as stable as the one made from chloranil. The

² Ber. d. chem. Ges., **21**, 461. Compare also **27**, 810.

chlordiphenoxyquinone (melting-point 169° – 170°) made from trichlorquinone, also forms a hemiacetal, but this is much less stable than that containing two atoms of chlorine. Even the dimethoxydiphenoxyquinone yielded a hemiacetal, but it was so unstable that it decomposed spontaneously almost as soon as it was formed. So that the stability of the hemiacetals seems to depend on the number and strength of the negative radicles attached to the benzol ring. It was not very probable, therefore, that a hemiacetal of quinone itself could be isolated, but yet we felt it was necessary to try the experiment; and this has established the fact that quinone is acted on by sodic ethylate, although the product—a green salt—has so far, resisted our attempts to purify it for analysis. Work with it is especially hard because of its very slight stability; it takes fire spontaneously, if dried in the air at ordinary temperatures; and although if dried first in hydrogen, it does not take fire on mere exposure to the air, it glows like tinder when heated to temperatures as low as 40° . After we had abandoned, for the present, the attempt to analyze the green salt, we succeeded in throwing some light on its composition by determining the proportion of quinone to sodic ethylate necessary to form it, as we found that each molecule of quinone takes up one molecule of sodic ethylate, but it must be left to future experiments to decide whether the product is really a hemiacetal.

In all the work so far described in this paper, only two of the atoms of chlorine in chloranil have been replaced by other radicles; we found, however, that the other pair of atoms of chlorine could be replaced by phenoxy groups, if the dichlorodiphenoxyquinone was treated with sodic phenylate, or if chloranil was acted on by four equivalents of sodic phenylate. The tetraphenoxyquinone thus formed, melted at 229° – 230° , and offered a rather striking resistance to the action of reducing agents, although zinc-dust and glacial acetic acid, converted it into tetraphenoxyhydroquinine, $C_6(OC_6H_5)_4(OH)_2$, melting-point 219° – 220° . Toward acids the tetraphenoxyquinone shows a marked stability, but by boiling with a strong solution of sodic hydrate, it was converted into the diphenoxanilic acid, $C_6(OC_6H_5)_2(OH)_2O_2$, which melts at about 276° .

Sodic methylate converts tetraphenoxyquinone into the dimethoxydiphenoxyquinone by replacing two of its phenoxy by methoxy groups; the substance melts at 171° . The corresponding diethoxydiphenoxyquinone, melting at 128° , was formed, instead of tetraphenoxyquinone, when chloranil was treated with sodic phenylate made from phenol and sodic ethylate in alcoholic solution. It is a noteworthy fact that bromanil acts differently with sodic phenylate made in this way, giving the dibromdiphenoxyquinone. One other case was observed of the substitution of all four of the chlorine atoms of chloranil. This was when the dichlorquinone dimalonic ester of Stieglitz was boiled with alcohol and sodic carbonate, as it was converted into diethoxyquinone dimalonic ester, melting at 115° . It is certainly strange that such a weak reagent should remove these two atoms of chlorine, which in other cases have seemed very firmly attached to the molecule. In all the reactions just described it is to be observed that the chlorine atoms or phenoxy groups, are replaced in pairs, and this fact also appears in much of the work with chloranil previous to ours. This replacement of the radicles two at a time can probably be connected with the para position of the two atoms of oxygen, which in this case serve to diminish the attraction of these radicles to the benzol ring, and thus make it possible to replace them, as in the case of tribromdinitrobenzol, $\text{CHBrNO}_2\text{BrNO}_2\text{Br}$ (melting-point 192°) where the loosening nitro groups are in the meta position, all three of the bromine atoms are replaced in many reactions.

EXPERIMENTAL PART.

Action of Potassic Phenylate on Chloranil.

In order to study this action, 25 grams of chloranil suspended in 50 cc. of water were treated with an aqueous solution of potassic phenylate, made from 12 grams of potassic hydrate and 25 grams of phenol, which gave the proportion of two molecules of potassic phenylate to one of chloranil. To obtain a good result in this process it was necessary that the chloranil should not be in too large crystals; if, therefore, the specimen used was well crystallized, it was reduced to the hydroquinone with sulphurous acid, and then oxidized with

nitric acid, which left it in a finely divided form easily attacked by the solution of potassic phenylate. The potassic phenylate was added in small portions at a time, and the first few drops imparted to the liquid a chrome-green color, which gradually changed to blue-black as more of the solution was added, until at last the whole became very dark blue or nearly black. In order to complete the reaction the mixture was heated on the steam-bath for thirty minutes, which changed the color from black to red. In the cold there were no signs of the formation of this red substance, but it began to appear as soon as the mixture was warmed. The solution was filtered, and the dark red solid remaining on the filter, after washing thoroughly with water and alcohol, was purified by crystallization from hot benzol until it showed the constant melting-point of 243° .

The analysis of the substance dried at 100° gave the following results :

I. 0.2138 gram substance gave on combustion 0.4692 gram CO_2 and 0.0637 gram H_2O .

II. 0.1510 gram substance gave 0.1206 gram AgCl (Carius).

	Calculated for $\text{C}_6\text{Cl}_2(\text{OC}_6\text{H}_5)_2\text{O}_2$.	I.	Found.	II.
Carbon.....	59.83	59.85		
Hydrogen.....	2.77	3.32		
Chlorine	19.67			19.75

From these results it is evident that the substance is dichlordiphenoxyquinone. The yield is very good, 25 grams of chloranil giving as a rule 26 to 30 grams of the new substance, that is, about 80 per cent. of the theoretical yield.

Properties of Dichlordiphenoxyquinone, $\text{C}_6\text{Cl}_2(\text{C}_6\text{H}_5\text{O})_2\text{O}_2$.—The substance crystallizes from benzol in beautiful red needles arranged in rosettes. It melts at 243° , and is very slightly soluble in alcohol even when hot, less so when cold; insoluble in cold and in boiling water; difficultly soluble in boiling benzol, and only very slightly soluble in the cold; it is sparingly soluble in cold chloroform, more easily in hot; slightly soluble in cold glacial acetic acid, but easily when the acid is boiling; in ether, ligroin, carbon disulphide, or acetone, it is insoluble. The three strong acids have no visible effect on it, hot or cold. It is readily saponified by a solution of sodic hydrate, forming chloranilic acid. It is not affected by sul-

phurous acid at 100° under the ordinary pressure, but is easily reduced to the corresponding hydroquinone by warming with hydriodic acid, or by the action of glacial acetic acid and zinc-dust.

Dichlordiphenoxyhydroquinone, $C_6Cl_2(C_6H_5O)_2(OH)_2$.

This substance was prepared by mixing dichlordiphenoxyquinone with hydriodic acid (boiling between 123° and 126°), and heating for some time on the steam-bath. The product formed by this reduction was purified by crystallization from boiling dilute alcohol (50 per cent.) until it showed the constant melting-point of 197° . The analysis of the substance dried at 100° gave the following results:

I. 0.2147 gram substance gave on combustion 0.4678 gram CO_2 and 0.0723 gram H_2O .

II. 0.1578 gram substance gave 0.1244 gram $AgCl$ (Carius).

	Calculated for $C_6Cl_2(OC_6H_5)_2(OH)_2$.	I.	Found.	II.
Carbon	59.51	59.41		
Hydrogen	3.31	3.73		
Chlorine	19.56			19.49

The change from the quinone to the hydroquinone is quantitative.

Properties of Dichlordiphenoxyhydroquinone.—It crystallizes from dilute alcohol (50-per cent.) in large colorless prisms, or in little needles very much branched, forming thick absorbent masses which melt at 197° – 198° , and are readily soluble in ethyl alcohol, methyl alcohol, or acetone; soluble in carbonic disulphide or hot glacial acetic acid; slightly soluble in chloroform, cold glacial acetic acid, or ether. It is insoluble in water, either cold or hot, benzol, or ligroin. Dilute or strong sulphuric acid or hydrochloric acid does not act on the dichlordiphenoxyhydroquinone even when hot. It dissolves in alkalis and is reprecipitated from the solution by acids. On long standing or boiling with sodic hydrate it is saponified, giving the sodium salt of chloranilic acid which separates in long dark carmine-red needles.

By the action of oxidizing agents, such as ferric chloride, dilute nitric acid, or potassic dichromate in acid solution, it is easily changed to the corresponding quinone.

Action of Aniline on Dichlordiphenoxyquinone.

The dichlordiphenoxyquinone was treated with aniline in the expectation of removing the two remaining atoms of chlorine. For this purpose 1 gram of dichlordiphenoxyquinone was mixed with 5 grams of aniline, and the mixture warmed on the water-bath for a few minutes. When cool, the large excess of aniline was removed by dilute sulphuric acid, and, after thorough washing, the dark-colored residue was purified by dissolving it in aniline, and then adding a small quantity of alcohol; in this way well-formed dark-brown crystals were obtained, melting at 287° – 290° , and therefore probably the dichlordianilidoquinone, the melting-point of which is given as 285° – 290° . This substance was first prepared and studied by O. Hesse¹, later by Knapp and Schultz.² To confirm this inference the crystals were dried at 100° and the chlorine determined:

0.1480 gram substance gave 0.1174 gram AgCl (Carius).

	Calculated for $C_6Cl_2(C_6H_5NH)_2O_2$.	Found.
Chlorine	19.70	19.61

The reaction therefore took an unexpected course, since the anilido groups replaced the two phenoxy radicles instead of the two atoms of chlorine.

Action of Sodium Malonic Ester on Dichlordiphenoxyquinone.

It has been shown in the preceding section that aniline removes the phenoxy groups instead of the atoms of chlorine from dichlordiphenoxyquinone. We therefore next turned our attention to the action of sodium malonic ester upon it, to see whether this reagent behaved in the same way. In order to study this reaction, 1 gram of dichlordiphenoxyquinone suspended in 10 cc. of absolute alcohol, was treated with a little more than two equivalents of sodium malonic ester, which was made by treating 0.15 gram of metallic sodium with about 10 cc. of absolute alcohol, and then adding 2 grams of malonic ester. On adding the sodium malonic ester, the solution turned very dark-blue, and on standing a dark-blue precipitate separated, which was filtered off and

¹ Ann. Chem. (Liebig), **114**, 306.

² Ibid. **210**, 187.

washed with alcohol, in which it is only slightly soluble. The precipitate dissolved readily in water, with a beautiful blue color, and on the addition of an acid a slightly yellow crystalline product separated, which was purified by recrystallization from boiling dilute alcohol, until it gave the constant melting-point 132° . After drying at 100° , it gave the following results on analysis:

I. 0.2180 gram substance gave on combustion 0.3880 gram CO_2 and 0.0994 gram H_2O .

II. 0.1654 gram substance gave 0.0964 gram AgCl .

	Calculated for $\text{C}_8\text{Cl}_2[\text{CH}(\text{COOC}_2\text{H}_5)_2]_2\text{O}_2$.	Found.	
		I.	II.
Carbon	48.68	48.53	
Hydrogen	4.46	5.06	
Chlorine	14.41		14.41

These results prove that the substance is dichlorquinonedimalonic ester. Four grams of the dichlordiphenoxyquinone gave a yield of about 1.5 grams of the malonic ester compound, that is, 27 per cent. of the theoretical yield.

It is evident that this body must be formed through the replacement of the two phenoxy groups by two malonic-ester radicles and, in fact, it was not hard to detect the phenol, which formed the secondary product of the reaction. For this purpose the alcoholic filtrate from the sodium salt of the malonic-ester derivative, after evaporation nearly to dryness, was diluted with water, and treated with a dilute acid, when the smell of phenol was very evident, and bromine-water gave a voluminous white precipitate. This easy replacement of the phenoxy groups by the malonic-ester radicles, even although the former are attached to a benzol ring, suggests other work in the same line, which will be undertaken in this laboratory.

This dichlorquinonedimalonic ester crystallizes from dilute alcohol in long, slender radiating needles of a yellow color, which melt at 132° , and are insoluble in cold or boiling water, soluble in cold or warm alcohol. It is not affected by weak oxidizing agents, but hydriodic acid reduces it to a white crystalline substance, which melts at 159° – 160° , the melting-point of the dichlorhydroquinonedimalonic ester discovered

by J. Stieglitz¹; our dichlorquinonedimalonic ester is therefore identical with that obtained by him from the direct action of sodium malonic ester on chloranil. Our indirect method of preparing it, however, gives a better yield than the direct method, 27 per cent. instead of 10 per cent. That we might not intrude on this field of research, already occupied by Stieglitz, we have confined our work on this substance to that necessary for establishing its identity.

Sodium Salt of Dichlorquinonedimalonic Ester,



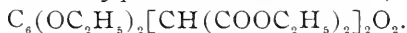
In order to prepare this salt the dichlorquinonedimalonic ester was dissolved in ether, and treated with rather less than the required amount of sodic ethylate in a strong alcoholic solution. The sodium salt separated at once as a blue precipitate, which was repeatedly washed with ether by decantation, and dried over sulphuric acid and paraffine until the weight remained constant, after which the sodium was determined with the following result:

0.2788 gram salt gave 0.0731 gram Na_2SO_4 .

	Calculated for $\text{C}_6\text{Cl}_2[\text{CNa}(\text{COOC}_2\text{H}_5)_2]_2\text{O}_2.$	Found.
Sodium	8.57	8.49

The sodium salt has a beautiful blue color, and is very easily soluble in water, giving a solution of a blue color as intense and striking as that of aniline-blue. It is somewhat soluble in alcohol, but insoluble in ether.

Diethoxyquinonedimalonic Ester,



In the first attempt to form the sodium salt of the dichlorquinonedimalonic ester, the substance was dissolved in absolute alcohol and boiled with an excess of dry sodic carbonate. When the sodic carbonate was first added, the alcoholic solution was colored dark blue; but after filtering out the excess of sodic carbonate and evaporating rapidly, the solution became nearly colorless, and left after the alcohol had been driven off a residue of almost white crystals, which were purified by crystallization from alcohol until the melting-point remained

¹ This Journal, 13, 38.

constant at 115°. The analysis of the substance dried over sulphuric acid and paraffine gave the following results:

0.2010 gram substance gave on combustion 0.4122 gram CO₂ and 0.1242 gram H₂O.

	Calculated for C ₆ (OC ₂ H ₅) ₂ [CH(COOC ₂ H ₅) ₂] ₂ O ₂ .	Found.
Carbon	56.25	55.93
Hydrogen	6.25	6.86

It gave no test for chlorine. These results prove that the substance is diethoxyquinonedimalonic ester, and it is certainly strange that this substance should have been formed from the corresponding dichlor compound by the action of sodic carbonate and alcohol, in view of the fact that these two atoms of chlorine in other cases have proved hard to replace. The substance crystallizes in beautiful yellowish white needles melting at 115°, which are insoluble in water, readily soluble in alcohol or ether.

Action of Sodic Methylate on Dichlordiphenoxyquinone—Dichlordimethoxyquinone Dimethylhemiacetal,

$$\text{C}_6\text{Cl}_2(\text{OCH}_3)_2(\text{OH})_2(\text{OCH}_3)_2.$$

In order to see whether the phenoxy groups in dichlordiphenoxyquinone would be removed by sodic methylate, as they were when it was treated with sodium malonic ester or aniline, 10 grams of the dichlordiphenoxyquinone were mixed with a methyl-alcohol solution of a little less than four equivalents of sodic methylate, made by treating 2.5 grams of metallic sodium with 60 cc. of methyl alcohol. The solution was warmed gently on the water-bath, and stirred constantly; soon a white crystalline substance began to separate, and the red color of the dichlordiphenoxyquinone disappeared entirely. The solution was filtered, the residue washed with a little alcohol, dissolved in water, filtered again, and then treated with dilute sulphuric acid in excess, which set free a white insoluble compound. The properties of this substance indicated at once that the reaction had not consisted in a simple replacement of the phenoxy by methoxy groups, as in that case the product must have been the dichlordimethoxyquinone discovered by Kehrmann,¹ which is red, melts at 141°–142°, and is

¹J. prakt. Chem., [2], 40, 370.

not insoluble in the common solvents. To prepare our new body for analysis it was filtered off, washed with water, alcohol, and then with water again; after which it was dissolved in dilute sodic hydrate, filtered, precipitated with dilute sulphuric acid, and washed thoroughly as described above. This treatment was repeated two or three times, until the substance was perfectly white and did not change color when washed with alcohol and ether. It was then dried for a short time over sulphuric acid and paraffine, and was analyzed with the following results:

I. 0.2410 gram substance gave on combustion 0.3459 gram CO_2 and 0.1064 gram H_2O .

II. 0.2005 gram substance gave 0.2943 gram CO_2 and 0.9720 gram H_2O .

III. 0.1920 gram substance gave 0.1851 gram AgCl (Carius).

IV. 0.2372 gram substance gave 0.2233 gram AgCl (Carius).

	Calculated for $\text{C}_6\text{Cl}_2(\text{OCH}_3)_2\text{O}_2(\text{CH}_3\text{OH})_2$.	I.	II.	Found. III.	IV.
Carbon....	39.87	39.13	40.02		
Hydrogen •	4.65	4.90	5.38		
Chlorine ..	23.59			23.83	23.28

These results indicate that the substance is a dimethoxydichlorquinone to which two molecules of methyl alcohol have been added. To confirm this view of its composition the sodium salt was prepared and analyzed as follows: An excess of the insoluble compound was added to a solution of sodic methyrate in a large quantity of methyl alcohol. As the sodium salt formed is soluble in methyl alcohol,¹ while the original compound is not, it was easy by filtering to obtain a pure solution of the salt, from which it was then precipitated by adding an excess of ether. The precipitate was repeatedly washed with ether by decantation, transferred to a weighed platinum crucible, dried over sulphuric acid and paraffine, and analyzed with the following results:

I. 0.2372 gram salt gave 0.0828 gram Na_2SO_4 .

II. 0.2887 gram salt gave 0.1025 gram Na_2SO_4 .

	Calculated for $\text{C}_6\text{Cl}_2(\text{OCH}_3)_2\text{O}_2(\text{CH}_3\text{ONa})_2(\text{CH}_3\text{OH})_2$.	I.	Found. II.
Sodium.....	11.24	11.31	11.50

¹In the preparation of the original substance the sodium salt was obtained as a precipitate, because the amount of methyl alcohol used was not enough to dissolve it.

As these analyses indicate that the salt contains two molecules of methyl alcohol of crystallization, an attempt was next made to determine the amount of volatile matter which it contained, with the following result:

0.3177 gram salt heated at 100° lost 0.0501 gram.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$.	Found.
Methyl Alcohol	15.65	15.77

Another sample of the sodium salt was then dried at 100° to a constant weight, and a sodium determination was made in the dry substance:

0.2422 gram salt gave 0.1018 gram Na_2SO_4 .

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2$.	Found.
Sodium.....	13.33	13.61

These results show that, by the action of sodic methylate upon the dichlordiphenoxyquinone in the first place the two phenoxy groups are replaced by two methoxy groups, and then two molecules of sodic methylate are added directly to the molecule of dichlordimethoxyquinone formed by the first part of the action. The proof that these two molecules of sodic methylate are attached to the carbonyl groups of the quinone has been given in the introduction to this paper, and the new substance therefore is dichlordimethoxyquinone dimethylhemiacetal.

Other Methods of Preparing the Dichlordimethoxyquinone Dimethylhemiacetal.

This body can be made also directly from chloranil by the action of sodic methylate. When one equivalent of chloranil was treated with five or six equivalents of sodic methylate dissolved in methyl alcohol, a green salt containing sodium separated. This salt was dissolved in water rendered alkaline by a little sodic hydrate, and the addition of a dilute acid to this solution produced a dirty-white precipitate, a portion of which was soluble in alcohol, while the rest remained undissolved. The insoluble part, after purification by dissolving in sodic hydrate and filtering, was precipitated again with dilute sulphuric acid, and washed with water and alcohol, after which it was dried in a desiccator, and the chlorine determined:

0.2060 gram substance gave 0.1962 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2$.	Found.
Chlorine.....	23.59	23.55

That this product was the same as that prepared from the dichlordiphenoxyquinone was shown also by its properties, which agreed with those observed for that substance, especially by its very characteristic reaction with dilute acids.

The other product obtained from the green salt formed by the action of sodic methyrate on chloranil was dissolved in the alcohol used in washing the dirty-white precipitate from dilute sulphuric acid; after evaporating off the alcohol, it was purified by recrystallization from dilute alcohol, and analyzed with the following result :

0.2094 gram substance gave 0.4841 gram AgCl (Carius).

	Calculated for $C_6Cl_4(OH)_2$.	Found.
Chlorine.....	57.25	57.16

As it melts at 235° , there can be no doubt that it is the tetrachlorhydroquinone, the melting-point of which is given by Sutkowski¹ as 232° . We are unable to determine at present whether this tetrachlorhydroquinone is due to a secondary reaction, or whether it proceeds from that by which the hemiacetal is made. Sodic ethylate does not act in this way with chloranil.

The dichlordimethoxyquinone dimethylhemiacetal is also formed when dichlordimethoxyquinone (melting at 141° – 142°) is treated with two equivalents of sodic methyrate dissolved in methyl alcohol.

Properties of the Dichlordimethoxyquinone Dimethylhemiacetal.

—It is a white amorphous solid, insoluble in all the common solvents. It is very easily converted into the red dichlordimethoxyquinone, melting at 141° – 142° , discovered by Kehrman.² This change can be effected by heat alone, since in the neighborhood of 160° it begins to take on a slight reddish color, which becomes darker very slowly at this temperature, but when heated to 195° or higher, the substance melts to a red liquid, at the same time increasing very much in volume and giving off many bubbles of gas consisting probably of the

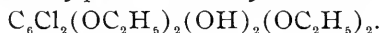
¹ Ber. d. chem. Ges., 19, 2316.

² J. prakt. Chem., [2], 40, 370.

vapor of methyl alcohol. The decomposition-point is not a definite one, as in different trials this action took place at temperatures sometimes as much as twenty or twenty-five degrees apart. An easier way to bring about this change is by treating the hemiacetal with dilute sulphuric acid or dilute hydrochloric acid, to either of which it shows itself remarkably susceptible, the decomposition taking place quantitatively, slowly in the cold, but quickly on warming. The ease with which it is attacked by dilute acids is its most striking property. Continued boiling with water or with dilute alcohol or glacial acetic acid brings about the same decomposition, as does also treatment of either the free substance or its sodium salt with benzoyl chloride in a sealed tube at 100° , methyl benzoate being the secondary product. Acetic anhydride decomposes it in the same way, but more slowly; on the other hand, neither methyl nor ethyl iodide acts on the sodium salt or the free substance. The formation of the benzoic ester of the substance is described below.

The hemiacetal is a weak acid, forming with sodic ethylate the white crystalline sodium salt, the method of preparation and analysis of which have been given above. This salt is soluble in water or alcohol, insoluble in ether. With argentic nitrate a white non-crystalline silver salt is formed, which is insoluble in water, and easily decomposed.

Action of Sodic Ethylate on Dichlordiphenoxyquinone—Dichlor-diethoxyquinone Diethylhemiacetal,



In order to study this action 10 grams of dichlordiphenoxyquinone were treated with an alcoholic solution of little less than four equivalents of sodic ethylate, which was made by treating 2.5 grams of metallic sodium with 60 cc. of absolute alcohol. When the sodic ethylate was first added there was no apparent action but, on standing, even in the cold, the red color of the dichlordiphenoxyquinone gradually disappeared, and a white crystalline sodium salt was formed. After warming gently on the water-bath to finish the reaction, the solution was filtered, the salt washed with alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in

excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and then with water again. In order to purify the substance further, it was dissolved in dilute sodic hydrate, filtered, precipitated again with dilute sulphuric acid, and washed thoroughly, as above. This treatment was repeated until finally the substance was perfectly white, and did not change color when washed with alcohol and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results :

I. 0.2205 gram substance gave on combustion 0.3802 gram CO_2 and 0.1304 gram H_2O .

II. 0.2017 gram substance gave 0.1614 gram AgCl (Carius).

	Calculated for $\text{C}_8\text{Cl}_2(\text{OC}_2\text{H}_5)_2\text{O}_2(\text{C}_2\text{H}_5\text{OH})_2$.	I.	Found.	II.
Carbon.....	47.06	47.02	
Hydrogen.....	6.16	6.57	
Chlorine	19.89		19.78

These results show that the action of the sodic ethylate on the dichlordiphenoxyquinone is analogous to that of sodic methylate, since two phenoxy groups are replaced by two ethoxy groups, and then two molecules of sodic ethylate are added directly to one molecule of the dichlordiethoxyquinone thus formed, giving the sodium salt of dichlordiethoxyquinone diethylhemiacetal. The yield of the sodium salt from 10 grams of dichlordiphenoxyquinone was usually a little less than 10 grams, and therefore, as the change from the sodium salt to the hemiacetal is nearly quantitative, we obtained over 75 per cent. of the theoretical yield.

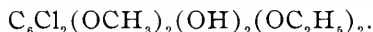
Properties of the Dichlordiethoxyquinone Diethylhemiacetal.

—It is a white amorphous solid, which dissolves slightly in alcohol, but is partially decomposed by this solvent, so that it cannot be recrystallized from it. It is essentially insoluble in all the other common solvents. By boiling with dilute sulphuric or hydrochloric acid it is decomposed, and the same reaction takes place more slowly when it stands with the dilute acid in the cold. The product of the action in either case is a light red body melting at 104° – 105° , after being purified by crystallization from alcohol, which is, therefore, dichlordiethoxyquinone, as this is the melting-point ascribed to

this substance by Kehrmann.¹ Stenhouse,² who discovered it, gives its melting-point as 107° ; but even by repeated recrystallization we have not been able to raise the melting-point above 104° – 105° , and therefore have come to the conclusion that Stenhouse's higher number must be due to an error. The white insoluble hemiacetal melts at 140° – 143° , or rather decomposes at this temperature, changing into the red dichlordiethoxyquinone, which then melts. From these properties it appears that the relationship between the diethyl and dimethylhemiacetals is of the closest sort.

Like the corresponding methyl compound the dichlordiethoxyquinone diethylhemiacetal has acid properties, forming with sodic hydrate a sodium salt. It shows toward sodic hydrate a stability in marked contrast to its susceptibility to the action of dilute acids, as it is necessary to boil it with a strong solution of sodic hydrate in order to saponify it to chloranilic acid. The sodium salt of the diethylhemiacetal is white and crystalline, readily soluble in water, slightly soluble in alcohol, and insoluble in ether. The dried salt is slowly decomposed on standing in a closed bottle for several weeks, alcohol is given off, and a solid product left which contains some sodic chloranilate and another body, or more than one, which we have not yet identified. The silver salt is insoluble, and has a slight brownish-yellow color. It is blackened by light, alcohol being set free. On warming with water a red substance is formed, probably chloranilic acid. Insoluble salts were also obtained with solutions containing barium, calcium, lead, or zinc, but they were not studied. The details of the preparation of the sodium and silver salts will be found under the preparation of dichlordiethoxyquinone tetraethylacetal, later in this paper.

Dichlorodimethoxyquinone Diethylhemiacetal,



This substance was made by treating 0.9 gram of dichlorodimethoxyquinone with an alcoholic solution of sodic ethylate made from 0.2 gram of metallic sodium and absolute alcohol. After warming the mixture for a few minutes, all the red

¹ J. prakt. Chem., [2], 40, 365.

² Ann. Chem. (Liebig), Suppl., 8, 14.

dichlordimethoxyquinone disappeared, and a crystalline sodium salt was deposited. The liquid was then cooled, the precipitate filtered out, washed with a little alcohol, and dissolved in water, in which it is completely and easily soluble. The aqueous liquid after filtration was treated with dilute sulphuric acid, which threw down a white bulky precipitate of the free hemiacetal, and this, after thorough washing with water, alcohol, and ether, was dried over sulphuric acid and paraffine, and analyzed with the following result:

0.1892 gram substance gave 0.1627 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2(OH)_2(OC_2H_5)_2$.	Found.
Chlorine	21.58	21.26

The dichlordimethoxyquinone diethylhemiacetal, like those hemiacetals which have been described already, is an amorphous white solid, essentially insoluble in all the common solvents. It is decomposed at temperatures between 140° and 160° , forming a red substance, probably dichlordimethoxyquinone, and it is easily saponified by dilute acids.

[To be continued.]

FROM PINENE TO CARVACROL.

BY JOHN L. MEAD AND EDWARD KREMERS.

The conversion of pinene into pinene nitrosochloride and of the latter into the so-called "nitrosopinene," is generally known. That the last mentioned compound has been misnamed, that it is not a nitroso derivative but an oxime, was demonstrated by Mr. Urban and one of us a year ago.¹ Although the abstract in the *Berichte*,² concluded with the sentence "Die Untersuchung des Oeles, vermuthlich eines Ketones, $C_{10}H_{14}O$, ist in Angriff genommen," Prof. A. v. Baeyer³ saw fit to ignore the work already accomplished, and to publish the results of some of his own investigations on the same subject. That the product of hydrolysis of the oxime⁴ $C_{10}H_{14}NOH$ is not a ketone but a phenol, was recognized shortly after the publication of the note already referred to,

¹ This Journal, 16, 404.

² Referate, 27, 793.

³ Ber., d. chem. Ges., 28, 646.

⁴ v. Baeyer supposes it to be a binitrosyl derivative.—*loc. cit.*

and as soon as sufficient material for experimentation had been prepared. That this phenol is carvacrol Prof. v. Baeyer has already stated, basing his conclusion upon a single reaction. Inasmuch as this conversion of nitrosopinene into carvacrol appeared to be of great importance, it was thought best not to be content with a single proof, but to obtain sufficient evidence to establish the identity of the resulting product, beyond all reasonable doubt. This had been accomplished before Prof. v. Baeyer's publication.

Hydrolysis of so-called Nitrosopinene.—The nitrosopinene is dissolved in concentrated hydrochloric acid and after solution has been effected, about one-half the quantity of water is added. The solution is then heated on a water-bath until the reaction, which is rather violent at first, is ended. The oil which separates is distilled with water-vapor, a small quantity of black resin remaining behind. The presence of hydroxylamine was easily ascertained. The yield was about 65 per cent.

The oily distillate, which was of a light reddish color, was dried with anhydrous copper sulphate and fractionated. More than 75 per cent. distilled within 2° , *viz.*, $230-232^{\circ}$. Most of this fraction distilled at 231.5° uncorr., or 236.7° corr., under a barometric pressure of 743 mm. A redetermination of the boiling-point of this fraction, under a pressure of 725 mm., gave 230.3° uncorr. and 235.6° corr., respectively.

The rectified oil was of a light yellow color and possessed a decided phenol odor. Its density at 20° was 0.9780. It was optically inactive. Its index of refraction was found to be $N=1.52128$, hence the coefficient of refraction $R_n =$

$$\frac{N^2-1}{(N^2+2)d} = 0.31151 +.$$

Attempts to crystallize the oil at ordinary temperatures failed. When exposed to a temperature below -100° , it formed a transparent amorphous solid. Upon rise of temperature the mass softened at about -40° , crystallized at from -20° to -18° , and melted at -0.5° .

Upon analysis the following results were obtained:

I. 0.2686 gram phenol yielded 0.7709 gram $\text{CO}_2 = 0.21024$ gram C, and 0.2359 gram $\text{H}_2\text{O} = 0.02621$ gram H.

II. 0.2733 gram phenol yielded 0.7853 gram $\text{CO}_2 = 0.21417$ gram C, and 0.2402 gram $\text{H}_2\text{O} = 0.02668$ gram H.

	Calculated for $\text{C}_{10}\text{H}_{14}\text{O}$.	I.	Found. II.
C	80.00	78.27	78.36
H	9.33	9.76	9.40
O	10.66		

The phenol is but sparingly soluble in water, but freely soluble in alcohol, ether, chloroform, etc. It is also soluble in solutions of the fixed alkalis of more than 2 per cent. strength, from which solutions it is precipitated upon the addition of acids.

Its aqueous solution is colored green by ferric chloride, and from this solution small crystals separate in the course of time, which melt at 145° – 147° . The oil heated with chloroform and caustic alkali, produces a crimson color fading to brown.

The transparent, prismatic crystals of the sulphonic acid melted at 57° – 58° . The barium and lead salts were prepared, and quantitative determinations of the metals and of water of crystallization were made. The results will be given in the table below.

From the sulphonic acid the nitro compound was also prepared. The clear, dried crystals melted at 114° – 116° . The melting-point remained practically unchanged upon recrystallization from hot petroleum-ether. Nitrogen determinations were made with the following results:

I. 0.3900 gram substance yielded 41.3 cc. gas at 23° and 736 mm. pressure $= 0.04628$ gram N $= 11.87$ per cent.

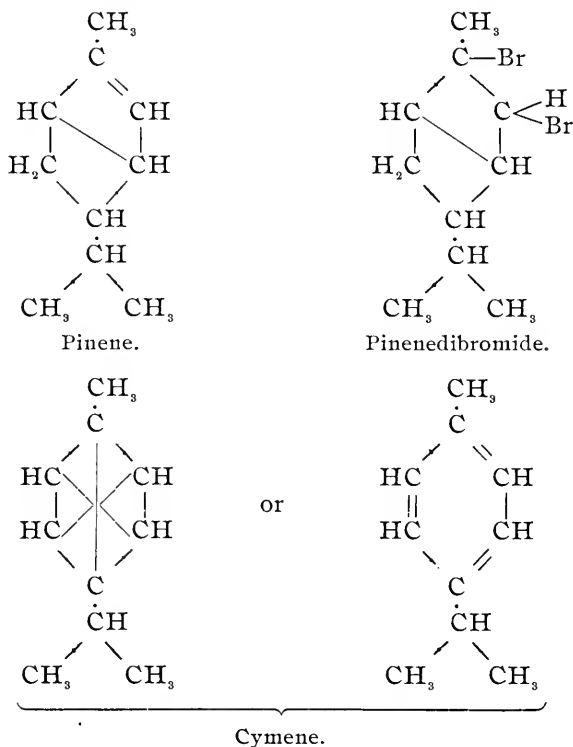
II. 0.5204 gram substance yielded 54 cc. gas at 20° and 742 mm. pressure $= 0.0615$ gram N $= 11.83$ per cent.

Dinitrocarvacrol, $\text{C}_{10}\text{H}_{11}(\text{OH})(\text{NO}_2)_2$, contains 11.66 per cent. nitrogen.

With bromine and iodine no crystalline substitution-products were obtained. These negative results as well as the positive results enumerated indicate beyond doubt that the phenol in question is *carvacrol* and not thymol, its isomer.

	Thymol.	Phenol from Pinene.	Carvacrol.
Boiling-point	228°-230°	235.6°	236°-237°
Melting-point.....	50°	-0.5°	0°
<i>d</i>	0.9689 at 24 $\frac{1}{4}$ °	0.9780 at 20°	0.9752 at 20°
<i>N</i>	—	1.52128	1.52344
<i>R</i>	0.31300	0.31151	0.31200
Melting-point of sulphonic acid....	98°	57°-58°	65°
Melting-point of dinitro compound.	55°-56°	115°	117°
	Per cent.	Per cent.	Per cent.
Percentage Ba in Ba-salt	20.5	20.10	19.97
Water of crystallization of Pb-salt...	9.74	12.19	11.90
Percentage Pb in Pb-salt.....	28.00	27.60	27.34

Wallach¹ has explained the formation of cymene from pinene dibromide, with the aid of the following formulas:

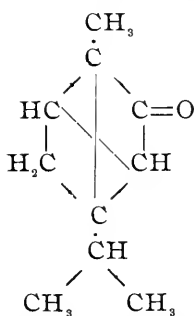
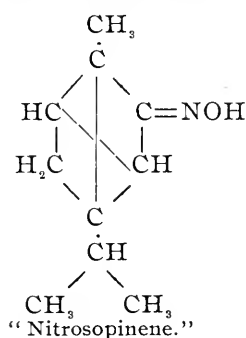
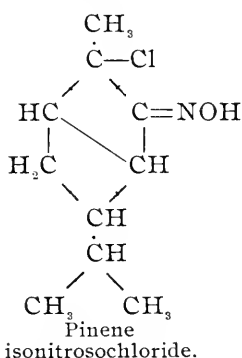
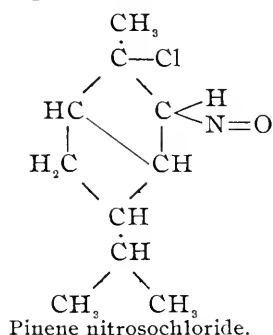
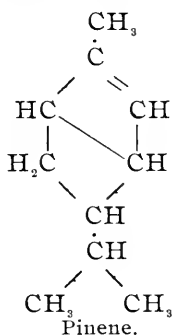


Being guided by the course of the reactions, which take place in the conversion of menthene to Δ^4 terpene-3-one,³

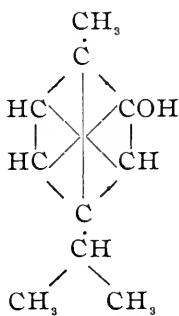
¹ Ann. Chem. (Liebig), 268, 213.

² Proc. Am. Pharm. Assoc., 42, 270.

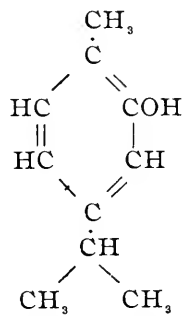
the conversion of pinene into carvacrol can be explained satisfactorily with the aid of Wallach's pinene formula—



Ketone from "Nitrosopinene."
Intermediate product
of hydrolysis.



or



Carvacrol, final product of hydrolysis.

Contribution from the Kent Chemical Laboratory of the University of Chicago.
ON HALOGEN ADDITION-PRODUCTS OF THE
ANILIDES.

[*Preliminary paper.*]

BY H. L. WHEELER.

This paper contains a description of the bromination of metanitroacetanilide. In this case I have succeeded in isolating a comparatively stable dibrom addition-compound, which is the first substance formed when bromine is added to the anilide. From this addition-compound the so-called substitution-product is then obtained by the separation of hydrobromic acid. This is the first halogen addition-product that has been obtained in the case of the anilides.

Experiments are now in progress in this laboratory which show that analogous halogen addition-products can be prepared from other anilides. A description of these will be given in a later paper. This preliminary notice, in the case of metanitroacetanilide, is given in order that I may reserve the field for myself.

These addition-products are especially interesting since they show that the process which is usually called substitution, in the case of the anilides, is really addition, then a separation of halogen hydride with the consequent formation of the so-called substitution-product.

Action of Bromine on Metanitroacetanilide.

When bromine is mixed with dry metanitroacetanilide the substances combine with evolution of heat but without giving off hydrobromic acid. When this mixture is strongly heated it melts with effervescence and torrents of hydrobromic acid are evolved. On cooling, if it has been carefully heated, the residue solidifies to a light yellow mass; this, on crystallizing once from benzene, gives pure parabrommetanitroacetanilide, melting at 143° . The base obtained from this by removing the acetyl group melts at 131° . If, on the other hand, the mixture is treated with sulphurous acid or ammonia, the halogen is quantitatively removed and metanitroacetanilide is recovered. Thus obtained, the anilide melts at 152° and the base at 114° .

These facts led the author to attempt the isolation of the bromine addition-product that is evidently formed here. The best results were obtained in the following manner: Metanitroacetanilide was dissolved in nitrobenzene, in which it is readily soluble, an excess of bromine was added, and the clear solution was then precipitated with dry ligroïn: a heavy translucent dark-red oil separated. The whole was transferred to a separatory funnel and the supernatant ligroïn solution, containing the nitrobenzene and excess of bromine, decanted. The oil was then shaken thoroughly three times, each time with over its own volume of dry ligroïn. A portion was then taken out by means of a pipette and immediately corked in a weighing-tube. After weighing the substance, the tube was uncorked and plunged into dilute ammonia. A bromine determination was then made in the usual way. [Analysis I.] The remaining portion of the oil was then shaken again with more ligroïn. It began to crystallize. A portion was removed and a bromine determination made. [Analysis II.] After shaking what remained again, the fifth time, with more ligroïn, considerable material separated in the solid condition. On exposing a portion of this oil to the air it immediately solidified. The material was separated as before and analyzed. [Analysis III.]

- I. 0.6392 gram substance gave 0.6922 gram AgBr.
- II. 0.4270 gram substance gave 0.4670 gram AgBr.
- III. 0.5067 gram substance gave 0.5565 gram AgBr.

	I.	Found. II.	III.	Calculated for $C_8H_8N_2O_3.Br_2$.
Br	46.1	46.5	46.7	47.0

In dry chloroform or glacial acetic acid containing bromine, the addition-product remains unaltered for days. It can be crystallized from these solvents. It then separates in the form of radiating bunches of flattened, transparent, bright yellow prisms. These melt with effervescence at 143° . The addition-product therefore has the same melting-point as the substitution-product. A specimen crystallized from glacial acetic acid containing bromine and rapidly pressed on paper, was then placed in a tightly corked weighing-tube for analysis.

0.3221 gram substance gave 0.3415 gram AgBr.

	Found.	Calculated for $C_8H_8N_2O_3.Br_2$.
Br	45.1	47.0

Specimens were obtained by preparing a hot saturated chloroform-solution of metanitroacetanilide, adding an excess of bromine and then allowing the whole to cool. An excess of bromine must be present, otherwise the unaltered anilide separates along with the addition-product. A crystalline product thus obtained was rapidly pressed on paper and dried on the water-bath. [Analysis I.] Another portion of the same was dried by exposing it for a short time to the air. [Analysis II.] A third portion was rapidly pressed on paper, and, in order to avoid decomposition by exposure, the material, which was still slightly moist with the mother-liquor, was immediately analyzed. [Analysis III.]

I. 0.3200 gram substance gave 0.3330 gram AgBr.

II. 0.2200 gram substance gave 0.2232 gram AgBr.

III. 0.3498 gram substance gave 0.3952 gram AgBr.

	I.	Found. II.	III.	Calculated for $C_8H_8N_2O_3.Br_2$.
Br	44.3	43.2	48.0	47.0

These analyses show that the substance is a dibrom addition-product. The low results are due to the fact that some bromine is lost in the process of drying. When the addition-product is exposed to the air it gives off bromine. A portion exposed for twenty-four hours in a desiccator over potash and sulphuric acid, contained only 37.4 per cent. of the halogen. The residue in the case of a specimen exposed in this manner for a week consisted of a mixture of substances, apparently metanitroacetanilide, parabrommetanitroacetanilide, and the hydrobromic acid addition-products of these (see below).

Hydrobromic acid is liberated from the addition-product, with consequent formation of parabrommetanitroacetanilide, on heating or on crystallizing it from water. Water removes hydrobromic acid in the cold. Metanitroacetanilide and bromine, in the proportion to form the dibrom addition-product, were mixed under water. The material was then immediately filtered and converted into the base as indicated below. On crystallizing this base from water it was found to

be pure parabrommetanitriline. This amounted to 64 per cent. of the calculated yield.

Cold concentrated nitric or sulphuric acid also separates hydrobromic acid from the addition-product. In these cases, however, the reaction takes place chiefly with displacement of bromine. A well crystallized specimen of the addition-product, obtained from a hot chloroform solution, was rapidly dried on the water-bath. On dissolving this in sulphuric acid drops of bromine sank to the bottom of the solution and fumes of hydrobromic acid escaped. The bromine was removed by means of a stream of air and the solution poured into ice-water. The substance that separated was crystallized from water, when yellowish white tables were obtained. These melted at 152° (not sharply). This material was, therefore, chiefly metanitroacetanilide; it, however, contained some parabrommetanitroacetanilide, as shown by qualitative tests for bromine.

Metanitroacetanilide is recovered from the addition-product and the bromine is quantitatively removed by means of the alkalis, ammonia, or sulphurous acid. Moist silver oxide also removes bromine. Metanitroacetanilide is also obtained when the addition-product is crystallized from strong alcohol. These reactions preclude the possibility that, in the formation of parabrommetanitroacetanilide, substitution first takes place and that the resulting hydrobromic acid remains combined with the anilide.

Parabrommetanitroacetanilide.—This compound was best prepared by treating the dibrom addition-product with water. When the substance thus treated was crystallized from hot water, it separated in the form of pale yellow needles or prisms. For analysis the material was dried at 100° and a bromine determination made according to the method of Carius:

0.2040 gram substance gave 0.1452 gram AgBr.

	Found.	Calculated for $C_8H_7N_2O_3Br$.
Br	30.3	30.8

If in the preparation of this compound an excess of bromine is employed and the whole warmed for some time, the acetyl

group is removed, and then *s*-tribrommetanitraniline is formed.

Parabrommetanitraniline ($\text{NH}_2, \text{NO}_2, \text{Br} : 1, 3, 4$).—This results when the above acetyl compound is boiled for a few minutes with alcohol and concentrated hydrochloric acid. On evaporating the alcohol and adding ammonia the base is precipitated. This, on crystallizing from hot water, gives very long, bright yellow slender needles, melting at 131° . This base is identical with the compound obtained by nitrating parabromaniline according to the method of Nölting and Collin.¹ A specimen thus obtained was converted into the acetyl compound. This melted at 143° and had the same properties as the compound obtained from the addition-product. The structure of the base obtained from the acetyl compound was confirmed by converting it into dibromnitrobenzene ($\text{NO}_2, \text{Br}, \text{Br} : 1, 2, 5$), according to Sandmeyer's² method. This base differs little in basicity from metanitraniline. Salts can readily be prepared by the usual methods. These are decomposed by water.

The *hydrochloride*, $\text{C}_6\text{H}_5\cdot\text{N}_2\text{O}_2\text{Br}\cdot\text{HCl}$, crystallizes in extremely long, slender, colorless needles.

0.3131 gram substance gave 0.1763 gram AgCl .

	Found.	Calculated for $\text{C}_6\text{H}_5\cdot\text{N}_2\text{O}_2\text{Br}\cdot\text{HCl}$
HCl	14.3	14.4

The *sulphate*, $(\text{C}_6\text{H}_5\cdot\text{N}_2\text{O}_2\text{Br})_2\cdot\text{H}_2\text{SO}_4$, crystallizes in long, slender, colorless needles. With only a few grams of material crystals over 5 cm. in length were obtained.

0.3282 gram substance gave 0.1410 gram BaSO_4 .

	Found.	Calculated for $(\text{C}_6\text{H}_5\cdot\text{N}_2\text{O}_2\text{Br})_2\cdot\text{H}_2\text{SO}_4$
H_2SO_4	18.0	18.4

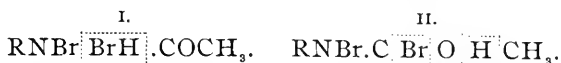
Theoretical Considerations.

No derivatives of the dibrom addition-product of metanitroacetanilide have yet been prepared, but the evidence thus far obtained in regard to its structure, indicates that the halogen adds itself to the benzene nucleus and not to the nitrogen of the anilide group. If it be assumed that the bromine adds itself to the nitrogen of the anilide group, the addition-product

¹ Ber. d. chem. Ges., **17**, 266.

² *Ibid.* **17**, 2652.

would then be a derivative of pentavalent nitrogen (I.) or, less probably, of the pseudo form of the anilide (II.)



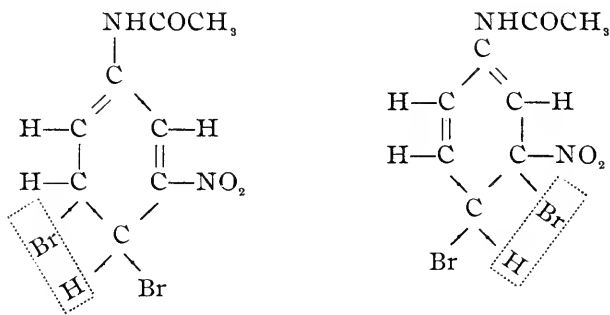
In the formation of the substitution-product from such compounds it would be expected that hydrobromic acid would separate from the anilide group as indicated by the dotted lines. The resulting compound, $\text{R} \cdot \text{NBr} \cdot \text{COCH}_3$, would then, by a molecular rearrangement give parabrommetanitroacetanilide, being an analogue of Bender's¹ chloracetanilide, $\text{C}_6\text{H}_5 \cdot \text{NCICOH}_3$, which readily undergoes this rearrangement. This however is not the case. Hydrobromic acid separates in a different manner. This is shown by the fact that bromine addition-products can be prepared from methylmetanitroacetanilide, $\text{C}_6\text{H}_4 \cdot \text{NO}_2 \cdot \text{NCH}_3 \cdot \text{COCH}_3$, and the dibrom derivative formed in this case readily separates hydrobromic acid. Here the possibility of such a separation of hydrobromic acid as indicated above is excluded. Therefore, on the assumption that the bromine combines with the nitrogen, it is not evident in what manner the substitution-product is formed.

On the other hand the formation of the substitution-product is readily explained if it is assumed that the bromine adds itself to the benzene nucleus. Moreover the latter assumption is rendered exceedingly probable by the fact that metanitroacetanilide combines with more than two atoms of bromine. This is shown by the following: When metanitroacetanilide is mixed with bromine in the proportion of one molecule of the anilide to four atoms of bromine, the substances combine with evolution of enough heat to effect the liquefaction of the mixture. This soon commences to solidify, and in a few minutes becomes a hard, reddish-colored, perfectly solid mass which can be pulverized and taken in the hand without injury to the skin. The bromine evidently combines with the anilide to form, presumably, a tetrabrom addition-product.

The formation of this higher bromine addition-product was frequently observed when a hot chloroform-solution of metanitroacetanilide was treated with a large excess of bromine.

¹ Ber. d. chem. Ges., 19, 2272.

It then separated along with the dibrom compound, imparting to the latter a deep red color. It is extremely unstable. When it is removed from the mother-liquor it immediately evolves bromine, in the form of vapor, decomposing rapidly into the bright yellow di-derivative. Various specimens obtained in this manner and pressed on paper until they gave no stain, gave analytical results showing that the substance contained bromine in excess of that calculated for the dibrom addition-product. These results varied from 48.0 to 56.8 per cent., of bromine. The calculated amounts of bromine in the dibrom and tetrabrom addition-products are 47.0 and 64.0 per cent., respectively. On account of the unstable nature of this higher addition-product, further attempts to isolate it were abandoned. These facts show however, that metanitroacetanilide combines with more than two atoms of bromine. It therefore seems probable that the unsaturated affinities between the carbon atoms of the benzene nucleus are the points where addition takes place, and that the bromine does not unite with the nitrogen of the amido group. Assuming Kekulé's formula for the benzene nucleus the structure of the dibrom addition-product would then be represented by either of the two following formulas:



The dotted lines indicate the manner in which parabrom-metanitroacetanilide then results by separation of hydrobromic acid. It is hoped that by a wider study of the halogen addition-products of the anilides further evidence in regard to their structure may be obtained.

Attempts were made to prepare the dibrom addition-product

by reversing the above operation and adding hydrobromic acid to parabrommetanitroacetanilide. Hydrobromic acid addition-products were readily obtained but these belonged to entirely different types. An isomeric addition-product, which probably has the structure of an ammonium salt, was obtained when 0.5 gram of parabrommetanitroacetanilide was dissolved in 20 cc. of a mixture of glacial acetic acid and ethyl acetate, and the solution saturated with dry hydrobromic acid gas. This compound separated in the form of beautiful colorless needles. Ammonia removed only one bromine atom in the form of hydrobromic acid. For analysis the substance was rapidly dried as far as possible by pressing on paper.

0.1662 gram substance gave 0.0882 gram AgBr.

	Found.	Calculated for $C_8H_7N_2O_3Br.HBr.$
HBr	22.8	23.8

The formation of another hydrobromic acid addition-product was observed when 3 grams of parabrommetanitroacetanilide were dissolved in glacial acetic acid and hydrobromic acid gas was passed into the solution for a short time. Colorless crystals, apparently rhombohedrons, separated. These were dried on paper.

0.2415 gram substance gave 0.0887 gram AgBr.

	Found.	Calculated for $(C_8H_7N_2O_3Br)_2HBr.$
HBr	15.8	15.6

These addition-products lose hydrobromic acid on exposure to the air. A specimen of the latter exposed for twenty-four hours contained 14.0 per cent. of hydrobromic acid.

It is noteworthy that when the higher bromine addition-products of metanitroacetanilide are heated or crystallized from water, not more than one molecule of hydrobromic acid separates from the acetyl compound. Hence all attempts to prepare a higher substitution-product than parabrommetanitroacetanilide were without success. A search was also made for isomeric monobrom derivatives that might be formed. No trace of these could be detected.

XIII.—SYNTHESIS OF DIPHENYLBIPHENYL AND ITS IDENTIFICATION AS BENZERYTHRENE.

BY ARTHUR A. NOYES AND ROLFE M. ELLIS.

The purpose of this investigation was to prepare synthetically the compound diphenylbiphenyl, $C_6H_5.C_6H_4.C_6H_4.C_6H_5$, and to determine by a comparison of its properties, whether, as might be expected, it is one of the products of the action of heat on benzene. It seemed probable that this substance might be obtained by the Fittig reaction, by the treatment of brombiphenyl with sodium, and accordingly, an attempt was made to prepare it in this way.

Biphenyl was made in the usual manner, by passing benzene through a red-hot tube. From this, brombiphenyl was prepared as described by Schultz.¹ It is to be noted that the body thus obtained is the para compound, since it yields parabrombenzoic acid on oxidation.²

30 grams of brombiphenyl were dissolved in three to four times that quantity of absolute ether, and an excess (5 grams) of thin cut sodium added. The mixture soon heated to boiling, too violent action being prevented by surrounding the vessel with cold water. After two or three days the insoluble residue was separated from the ethereal solution by filtration. The solution was found to contain only unchanged brombiphenyl, and was used as the solvent for the brombiphenyl in the next sodium treatment. The residue was repeatedly extracted with hot water to remove the sodium bromide and excess of sodium. It was then dried and treated with successive quantities of cold benzene, (200 cc. in all), which dissolved much the larger portion. By the addition of alcohol to this benzene solution, there was precipitated a brown flocculent substance insoluble in ether, chloroform, and petroleum-ether, but very soluble in benzene and carbon bisulphide. All attempts to purify it by crystallization, subli-

¹ Ann. Chem. (Liebig), **174**, 207.

² *Ibid.* **174**, 209.

mation, and distillation failed. The residue insoluble in benzene was of a dirty white color. It was found to sublime at a high temperature, and was purified between watch-glasses in this manner.

The sublimate was pure white, and in the form of large crystalline leaflets. It was proved to be pure diphenylbiphenyl by combustion and by a vapor-density determination, made by the Victor Meyer method, in the vapor of boiling phosphorus pentachloride, (520°).

0.1364 gram substance gave 0.4684 gram CO_2 and 0.0735 gram H_2O .

0.1404 gram substance gave 11.70 cc. air, measured over water at 27° and 759 mm.

	Calculated for $\text{C}_{24}\text{H}_{18}$.	Found.
C	94.12	93.65
H	5.88	5.99
Vapor-density	10.64	10.57

From the constitution of the brombiphenyl used, it follows that the phenyl groups occupy the para positions with respect to the central bond.

The yield obtained was in all cases very small, amounting to only five per cent. of the theoretical.

Several attempts were also made to prepare the body by the action of sodium on brombiphenyl in boiling benzene solution, but entirely without success. The product consisted wholly of the brown flocculent substance referred to above, as precipitated by alcohol from the benzene extract.

The melting-point was accurately determined by heating portions of the substance enclosed in sealed capillary tubes, in a flask in the vapor of boiling diphenylamine, the external pressure, and consequently the boiling-point, being gradually increased until the substance liquefied. The temperature was then noted by means of a tested thermometer wholly immersed in the vapor. The melting-point was found to be 317° .

The substance distilled without decomposition under a pressure of 18 mm. at 428° (roughly determined with a mercu-

rial thermometer). Its behavior during the heating in the vapor-density determination, showed that its boiling-point under ordinary pressure is below 520° , and that it is stable at that temperature.

The substance is completely insoluble in boiling alcohol, ether, chloroform, and carbon bisulphide, and in cold benzene. It was but slightly soluble in boiling benzene, one part requiring more than one hundred parts of the solvent.

It is of interest to compare these properties with those of the isomeric substance, *s*-triphenylbenzene, which has been previously prepared by various investigators. The latter substance boils at 459° at 717 mm. (Crafts), melts at 170° , and is soluble in benzene.

It now remains to determine whether diphenylbiphenyl is produced by the action of heat on benzene. It is evident that it might result from a condensation of biphenyl in a manner similar to that by which this substance is formed from benzene.

A most thorough study of the high boiling hydrocarbons thus formed from benzene has been made by Schmidt and Schultz.¹ Of these, the one which they named benzerythrene agrees closely in properties with our hydrocarbon; for the analysis of it corresponded to the formula $C_{24}H_{18}$; it melted at 308° , boiled far above 360° , was insoluble in alcohol, and slightly soluble in boiling benzene, from which it crystallized on cooling. There is therefore, no doubt that the two substances are identical, and consequently that paradiphenylbiphenyl is produced by the action of heat on benzene. It seems probable that this substance might be obtained in considerable quantity by passing biphenyl through a red-hot tube.

REVIEWS.

CELLULOSE: AN OUTLINE OF THE CHEMISTRY OF THE STRUCTURAL ELEMENTS OF PLANTS WITH REFERENCE TO THEIR NATURAL HISTORY AND INDUSTRIAL USES. By C. F. CROSS and E. J. BEVAN. London and New York: Longmans, Green & Co., 1895. 310 pp., 14 plates.

This work will prove a revelation even to those who are more or less familiar with the subject. It removes cellulose

¹ Ann. Chem. (Liebig), 203, 118.

from the position of an indefinite and loosely characterized substance, to that of a definite chemical body with characteristic reactions, and even offers some very clever theories as to its constitution. The authors have skillfully compiled the important features of the present knowledge of the subject, avoiding the repetition of much that is trite, and to this have added an account of their own extensive investigations. The treatise is a thoroughly scientific one, but embodying many practical ideas and frequently pointing out possible applications of the results of investigations to some of the many industries based upon cellulose and vegetable fibres. Indeed, nearly one-third of the book is devoted to a discussion of the experimental and applied phases of the subject.

At the outset the authors differentiate sharply between cellulose and much that goes by that name. Plant fibres are not necessarily composed of the typical cellulose, as is shown by their characteristic reactions. In general such materials are divided into two broad classes: the true celluloses, typified by cotton-fibre, and the compound celluloses of which the most important representatives are the lignified plant tissues or fibres, jute-fibre being studied as the type.

Cellulose proper possesses definite composition: carbon, 44.2 per cent.; hydrogen, 6.3 per cent.; and oxygen, 45.9 per cent.; corresponding to the formula $C_6H_{10}O_5$. It presents characteristic hydration-phenomena, and exists in the plant in all stages of hydration, varying in general with age. It is soluble in a variety of reagents, from which it may often be precipitated without essential change. This solution is regarded as being due to the formation of compounds of the nature of salts, between the solvents and the hydroxyl groups of opposite character in the cellulose molecule. In its capacity of a polyhydroxy body, cellulose forms several compounds with dilute acids and alkalies. As a derivative of one of these compounds, the alkali cellulose xanthate, discovered by the authors and described by them elsewhere, is one of the most important. Other definite compounds are the acetates, benzoates and nitrates, all of the nature of esters or ethers, and indicating the existence of hydroxyl groups in the molecule. Cellulose also forms with sulphuric acid a series of compounds of great variety and complexity. The cellulose molecule is decomposed by hydrolytic agents, by oxidation, by ferments, and by destructive distillation. No direct synthesis of cellulose has been accomplished or seems likely to be, but attention is called to the formation of cellulose from bodies of simpler molecular structure in the case of the ropy fermentation of beet-juice and the similar product of the vinegar ferment. Based upon these studies, the authors present their

conclusions in which they regard cellulose as an anhydro aggregate of dextrose or aldose molecules, $C_6H_{12}O_6$. In this aggregate the carbonyl groups are suppressed, and may be set free by the action of acids (hydrolysis). Resolution by fusion with alkalis into ultimate products of which acetic acid amounts to about 30 per cent., indicates that the grouping $CO.CH_3$ is an important one. The negative or indifferent characteristics of cellulose show it to be a saturated compound. Synthetical reactions such as the formation of acetates, nitrates and benzoates, indicate four hydroxyl groups in the original unit molecule $C_6H_{10}O_6$, capable of reacting without disturbing the original configuration. The authors are inclined to think that the arrangement of the carbon atoms is a cyclic one, pointing out the significance of the fact that so many bodies of this class are derived either directly or indirectly from fibre or cellulose-like materials.

Compound celluloses are modifications of the true celluloses in which the latter have been subjected to the action of lignification, suberisation, or conversion into mucilage. There are many forms of such compounds of which the most common and important is the ligno-cellulose typified by the fibre-substance of jute. The authors find this fibre-substance to be a compound and not an encrusted cellulose. It is capable of being decomposed into several groups of characteristic bodies, an outline of which is best shown as follows:

Ligno-cellulose.			
Cellulose.		Lignone (non-cell.)	
Cellulose α Containing oxidised groups.	Cellulose β Containing $O.CH_3$ groups.	Furfural-yield- ing complex and secondary $O.CH_3$ groups	Keto-R- Hexene groups and constituents: CH_2CO residues.

The ligno-celluloses are characterized by a higher percentage of oxygen than the true celluloses, with the properties of an unsaturated compound containing C_6 -rings of a ketone or quinone character. Of the ligno-celluloses, two important reactions are discussed in detail, *viz.*, the reaction with chlorine, and the formation of furfural. These reactions are given by one or the other of the complexes above referred to. The chlorine reaction is apparently a direct addition of the halogen, producing a compound of definite composition. The reaction occurs with that portion of the ligno-cellulose commonly designated as lignin, and seems to be identical with the action of chlorine upon a quinone. Other constituents of the compound celluloses yield, upon distillation with strong hydrochloric acid, furfural. The authors conclude that two such constituents are capable of this change without definite-

ly pointing out their relation. One of these is the pentosan group and the other an oxycellulose group, without any apparent relations to the pentoses. It is significant however that, wherever the furfural reaction has been used as an indicator, and has been given with sufficient distinctness to warrant further investigation, it has been possible to prepare and isolate from the material appreciable quantities of the pentose sugars. There is doubtless some connection not yet well understood between all of the constituents of the compound colluloses which yield furfural.

The authors' theory of the origin and relation of the different kinds of cellulose is, that the true cellulose is an aggregation of simple carbohydrate molecules, that the so-called processes of lignification, etc., are really degrees of oxidation by which the molecular equilibrium of the true cellulose is disturbed. The resulting oxycelluloses are unstable, and tend to form closed-ring derivatives (furfural, lignone, keto-R-hexene bodies). The cellulose on the one hand, and the cyclic derivatives on the other, are connected by intermediate products which may be converted into cellulose-like bodies, into substances of low molecular weight, or into closed-ring compounds. There is in lignification a constant tendency toward cyclic compounds, in evidence of which the authors repeatedly refer to the secretion of aromatic derivatives and the formation of such products by destructive distillation of coal or wood. It is also pointed out in an interesting way, that cellulose is a non-nitrogenous excreted substance, and, so far as the plant is concerned, dead material.

The work is upon advanced ground and presents enough of fact and experimental data, to warrant the wholly plausible theories offered. To say that the latter will prove infallible is too much. The authors have, however, contributed the most valuable work upon the important subject of cellulose and plant fibres, in existence; a work which will serve as a valuable reference-book for a long time. In the light of so much that is excellent, it is out of place to call attention to minor criticisms, of which, indeed, few are to be found.

The paper upon which the book is printed, deserves special notice, being made from "normal" cellulose of enduring quality.

W. E. STONE.

HANDBUCH DER STEREOCHEMIE. Edited by DR. C. A. BISCHOFF, Professor of General Chemistry at the Riga Polytechnic, with the collaboration of DR. PAUL WALDEN, Professor of Physical and Analytical Chemistry. Two vols. With 250 wood cuts and the portraits of Pasteur, Le Bel, and van't Hoff. Frankfurt a. M.: H. Bechhold. Vol. II, pp. 449-1060+xvi. 1894.

The first volume of this work has been already noticed in

these pages.¹ The second volume maintains the essentially cyclopædic character of the book, of which the first 200 pages are occupied with a continuation of the systematic enumeration of the cases of geometrical isomerism, with full references to the literature. Inorganic compounds occurring in more than one modification are included here. Criticisms and references to the editor's own views are rare, and this part of the book is intended for reference rather than for reading. At the close of the book is a valuable appendix (pp. 833-1026), which brings the references up to the year 1894. In the intermediate division, which deals with the influence of space-relations in chemical reactions, the treatment becomes more characteristic and of more immediate interest. Here the editor becomes author, and the *Handbuch* merges into the *Lehrbuch* and becomes quite readable. The first chapter of this section deals with ring-formation. Stereochemistry has long since pointed out that the tendency to this form of linkage depends not only on the affinity of the atoms composing the ring, but on their number, and their relative positions prior to the closing of the ring; and here we have brought together for the first time interesting proofs that the nature of the atoms composing side-chains has an important influence. There follows an enumeration of all the known ring-systems, including inorganic rings. The configuration of benzene and hexamethylene is not discussed, references only being given, "because the question is not definitely settled." If this rule had been adhered to throughout, the book would have been much shorter, but we should have lost all reference to Prof. Bischoff's hypothesis of dynamic isomerism, which here begins to emerge from the haze which has hitherto enshrouded it. "According to the principle of the dynamical hypothesis, that one of two possible configurations results (*ceteris paribus*) in greater quantity, which allows the freest possible oscillation of the components of the molecule in the conditions of the experiment" (p. 777). Further, these oscillations are supposed to be rotations about the valence-axes. Followed out on suitable—presumably tetrahedral—models, these rotations are seen to result in some cases in "collisions," and reactions which cannot take place without a collision will not take place at all; hence, "abnormal reactions." For example, where we should expect to form only

$$\begin{array}{ccc} \text{CH}_3 & \text{CH}_3 & \\ \text{RC} \text{---} & \text{CR} & \end{array}$$

we get also

$$\begin{array}{ccc} \text{CH}_3 & & \text{H} \\ \text{RC} \text{---} & \text{CH}_2 \text{---} & \text{CR} \\ \text{CH}_3 & & \text{CH}_3 \end{array}$$

because this configuration allows more room for the oscillations of the

¹ See this Journal, 16, 475.

methyl groups. But as the usual models are defective, in that they do not show the distance of the atoms apart, deductions drawn from their collisions will often be wrong, and the models must be altered in accordance with the results of experiment till their indications agree with the facts. Moreover the oscillations will be modified by change of temperature, and the valence-axes, about which the oscillations take place, are supposed by many chemists to vary in direction—though on this point the author's views are not stated.

It seems difficult to devise crucial tests for a hypothesis of such an accommodating nature, and this is perhaps the reason that it has received scant attention from stereochemists. Perhaps the most definite indication of the theory is that like groups require more space than unlike groups, because, their orbits being similar, they are more likely to collide; so that if in the above formulæ one or two methyl groups were replaced even by the larger phenyl group, the first configuration might alone result, the phenyls being too far from the central carbon atoms to collide with the methyls.

Further developments of the dynamic hypothesis appear also in the chapter devoted to the limits of general reactions: "It is often observed that when a reaction takes place involving the compounds at the beginning of a homologous series a by-product results; but when we use a member of the series possessing a certain complexity the proportion of the by-product increases, and, as we ascend the series, it predominates, becoming the main product" (p. 817). This phenomenon may be brought about by the interaction of groups appearing in the structural formula to be far apart in the molecule, but which must be supposed to be in reality near together.

The complete explanation of these abnormal reactions may be far distant, but it is evident that Prof. Bischoff has taken the first steps towards it by thus collecting and classifying them. That there is something "unsatisfying" in this part of the book cannot be denied; just as we think one phenomenon is about to be "explained" the subject is dropped and another is hurried into view. We have neither a simple statement of facts nor a systematic review of them in the light of a completed theory. But this is perhaps the fault rather of the present state of stereochemistry than of the author.

In fact, since the grand generalizations of Van 't Hoff and Le Bel, stereochemical theory has been rather an aspiration than a fulfillment. Facts have multiplied apace, and useful working-hypotheses have not been wanting, but when we leave the ground which those chemists have made classic, we

find no longer the coherence, the harmony, the unity which facts present when viewed in the light of a theory which has kept pace with them. If Prof. Bischoff finds himself at present unable to supply this theory he does the next best thing in making us feel the lack of it. To decline to assume a virtue when our science has it not, to show shortcomings as well as advances, hidden weakness in the midst of apparent strength—these must be accounted essential merits in a scientific author writing on his special subject.

Few chemists will fail to find this book helpfully suggestive, and those who are specially interested in its subject will find it indispensable. Its value would be enhanced if we could be assured that appendices would from time to time be issued bringing the references to the literature up to date.

It must be observed that the book is not free from the misspelling of English names so common in German chemical literature. Thus we have on p. 15, Tail for Tait; on p. 92, Bush and March for Burch and Marsh; and on p. 995, Eilvart for

EILOART.

ELEMENTS OF QUALITATIVE AND QUANTITATIVE ANALYSIS. By G. C. CALDWELL, B.S., PH.D., Professor of General and of Agricultural Chemistry in Cornell University. Third Edition, revised and enlarged. Philadelphia: P. Blakiston, Son & Co.

“In this work the author has brought together what has already been published, separately, in the ‘Manual of Qualitative Chemical Analysis,’ by himself and Dr. S. M. Babcock, and the ‘Notes on Chemical Analysis’ by himself alone; he has added thereto, much matter on qualitative analysis, all of Parts III. and IV. on quantitative analysis, and nearly all of Part V.” (Extract from preface). The material of the work is arranged under five heads: Part I. treats of the “Processes of Analytical Chemistry and Some of the Products of Its Operations;” Part II. is a “Systematic Course of Qualitative Analysis;” Part III. is devoted to the “Operations of Quantitative Analysis;” Part IV. contains “Examples for Practice in Quantitative Analysis;” and Part V. is given up to “Miscellaneous Matter,” such as lists of apparatus and reagents, special directions for the use of the former and the preparation of the latter, tables, etc.

This work is justly open to one criticism which applies equally well to nearly all the present-day “laboratory guides,” namely, that it offers the student no practice or discipline in the methods of Physical Chemistry. The great educational value of these methods can scarcely be questioned, and they should not be ignored in any work which is offered the student for his guidance in the laboratory.

H. N. M.

THE ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY, AND BLOWPIPE ANALYSIS, from a Practical Standpoint, Including a Description of all Common or Useful Minerals, the Tests necessary for their Identification, the Recognition and Measurement of their Crystals, and a Concise Statement of their Uses in the Arts. By ALFRED J. MOSES, E.M., Ph.D., Adjunct Professor of Mineralogy, Columbia College, School of Mines; and CHARLES LATHROP PARSONS, B.S., Professor of General and Analytical Chemistry, New Hampshire College. New York: D. Van Nostrand Co.

Part I. treats of crystallography, one chapter being given to general principles, six chapters to the 6 Systems of crystallization, one to the measurement of crystal angles, and one to the clinographic projection of crystal figures. Part II., including chapters X–XIII., is devoted to blowpipe analysis. Part III., including chapters XIV–XXXI., treats of descriptive mineralogy, the arrangement of the species being according to what may be called the leading chemical constituent. Part IV., chapter XXXII., is made up of tables designed to facilitate the recognition of the commoner minerals, either by their physical properties or by their conduct before the blowpipe. The style of the work is to be commended for its clearness, and the treatment of the subject is adequate to the needs of the class of students for which the book was written. H. N. M.

OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN. Leipzig: W. Engelmann.

Attention was directed in this place over a year ago¹ to Ostwald's valuable series of reprints of classical papers taken from the literature of the exact sciences. Since that time several volumes have appeared which will be of general interest to the readers of this JOURNAL; the following especially because of their bearing upon important departments of physical chemistry:

No. 40. Zwei Abhandlungen ueber die Waerme: Lavoisier und Laplace—*M.* 1.20.

No. 42. Das Volumgesetz gasförmiger Verbindungen: Humboldt und Gay-Lussac—*M.* 0.60.

No. 44. Das Ausdehnungsgesetz der Gase: Gay-Lussac, Dalton, Dulong und Petit, Rudberg, Magnus, Regnault—*M.* 3.00.

No. 45. Elektrochemische Untersuchungen: Davy—*M.* 1.20.

No. 52. Die Kräfte der Elektrizität bei der Muskelbewegung: Galvani—*M.* 1.40.

No. 58. Chemische Abhandlung von der Luft und dem Feuer: Carl Wilhelm Scheele—*M.* 1.80.

These convenient little volumes are issued in a neat, flexible binding, and at prices which are designed to bring them within the reach of everyone. J. E. T.

¹ This Journal, 16, 157.

NOTE.

HELIUM.

The announcement made several months ago¹ of the discovery in the mineral "clèveite" of the gas which produces the line D_3 in the spectrum of the solar chromosphere, naturally excited widespread interest. The following data have been abstracted from a paper² read by Prof. Ramsay before the (London) Chemical Society, and will give some idea of the present state of the work of investigation.

Palmieri³ states that a lava-like substance ejected from Vesuvius, gave a spectrum showing the line D_3 ; he made no further examination of the substance to prove the identity of its constituent with solar helium. Hillebrand⁴ examined a number of uraninites from which gas was evolved; this gas he took to be nitrogen simply, whereas that element was present to the extent of only about 10 per cent.—a quantity sufficient, however, to mask many of the characteristic properties of helium. In the search for substances which would combine with argon, Ramsay was led to examine the gases given off on heating clèveite and certain related minerals, and has been able to prove that they consist, in great part, of helium.

About thirty minerals were examined; of these about half gave gas-mixtures in which the quantity of helium ranged from a mere trace to the point where it was practically the sole constituent. Many of these minerals contain uranium as an essential constituent—one, pitchblende, being practically pure uranium oxide,—but by no means all: yttrium and thorium are frequently constituents of minerals yielding helium under the influence of heat. The manner in which the gas is held by the mineral is unknown. Experiments in which uranium oxide was heated in contact with helium, or uranium itself in a mixture of helium and oxygen, and the apparatus allowed to cool, gave only negative results: helium was not absorbed. Similar experiments are still to be made with the oxides of thorium and yttrium, and with a mixture of these with uranium oxide.

The helium evolved from these minerals was frequently mixed with hydrogen; this was removed with the aid of hot copper oxide, or of metallic palladium—the latter reagent being used in certain cases to decide the question whether the

¹ W. Ramsay: Proc. Roy. Soc., 58, 65; etc.

² Ramsay, Collie and Travers: Proc. Chem. Soc., 1895, 684.

³ Rend. Acc. Napoli, 20, 233.

⁴ Bull. U. S. Geol. Survey, 78, 43.

hydrogen was or was not in combination. Nitrogen was also a usual constituent; it was removed, as in the case of the purification of argon, with hot magnesium, or by sparking with an excess of oxygen over a solution of caustic soda, the oxygen residue being afterwards removed with the aid of potassium pyrogallate. The densities of the several specimens of the gas, obtained from different sources or by different methods, averaged 2.18, the density of hydrogen being taken as the unit; after being mixed and submitted to further processes of purification, the density, determined with the aid of a larger bulb, was found to be 2.218. After circulation over hot magnesium and copper oxide the density was finally reduced to 2.133. Determinations of the wave-length of sound in the purified gas gave, as the ratio between the specific heats, the figure 1.632 and, finally, with the gas whose density had been found to be 2.133, the figure 1.652, the theoretical figure for a monatomic gas being 1.66.

"In the case of argon the purest specimen obtained gave for the ratio 1.659; and, as remarked,¹ not much dependence can be placed on the accuracy of the last figure.

"The result of these experiments goes to prove that the density of the gas named helium is not less than 2.13, and that it has the same claim to be considered a monatomic gas as mercury gas; or if it is a mixture, it must be a mixture of monatomic gases."²

One volume of water was found to be capable of dissolving only 0.0073 volume of helium, the lowest coefficient on record. Alcohol and benzene do not dissolve the gas at all. Prof. Olszewski is at present engaged in experiments to determine the critical constants of pure helium. The refraction-coefficient has been determined by Lord Rayleigh.

The study of the spectrum of helium by Mr. Crookes, has led to some very interesting results, a notable one being, that "at least two of the lines in the spectrum of helium, seen with a wide-dispersion prism, are coincident with two of the argon lines. These occur in the red, and comprise one of each of the two pairs of characteristic argon lines. This observation has been frequently repeated, using for the purpose spectroscopes of different dispersive power, and throwing into the field both spectra at the same time, with an exceedingly narrow slit; and we may say that if not absolutely identical, the lines are so near that it is not possible, with the means at our disposal, to recognize any difference in position. But the relative brilliancy is by no means the same. One of the argon lines, rather faint, is coincident with the prominent red of the

¹ Phil. Trans., 1895, 52.

² Ramsay, Collie and Travers: *Loc. cit.*, 696.

helium spectrum, and one of the strong red argon lines is coincident with a faint red line in the helium spectrum."¹

In concluding this paper the authors say: "It cannot be doubted that a close analogy exists between argon and helium. Both resist sparking with oxygen in presence of caustic soda; both are unattacked by red-hot magnesium; and, if we draw the usual inference from the ratio between their specific heats at constant volume and at constant pressure, both are monatomic gases. These properties undoubtedly place them in the same chemical class, and differentiate them from all known elements."²

"How does argon happen to occur in the air and helium only in minerals? Why is helium not present in air?"

"A satisfactory answer to this question is, we think, contained in a paper by Dr. Johnstone Stoney.³ He there shows that were hydrogen to be present in air (and it might be present, in spite of the oxygen with which it would be mixed, for a small quantity would surely escape combination), it would, in virtue of the velocity of its own proper molecular motion, remove itself from our planet, and emigrate to a celestial body possessing sufficient gravitational attraction to hold it fast. Dr. Stoney suggests this explanation to account for the absence of an atmosphere and of water-vapor on the moon, and for the presence of an atmosphere of hydrogen on the sun. It would also account for the absence of helium in our atmosphere, and for the presence of the chromopheric line D₃. Of course if an element can form compounds, or if it is absorbed by solids, as helium appears to be, it will, like hydrogen and helium, be found on the earth."⁴

Finally, the authors suggest, as the only explanation of the facts known to them, that argon and helium are both mixtures, and that they contain a common constituent. Experiments having for their end the determination of this question, are already in progress.

W. W. R.

¹ Ramsay, Collie and Travers: *Loc. cit.*, 1895, 698.

² *Ibid*, 699.]

³ Chem. News, 71, 67.

⁴ R., C., and T.: *Loc. cit.*, 700.

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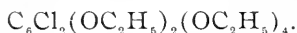
Contribution from the Chemical Laboratory of Harvard College.

LXXXVII.—ACTION OF SODIC ALCOHOLATES ON CHLORANIL. ACETALS DERIVED FROM SUBSTITUTED QUINONES.¹

BY C. LORING JACKSON AND H. S. GRINDLEY.

[Continued from page 607.]

Dichlordiethoxyquinone Tetraethylacetal,



It has already been stated that ethyl or methyl iodide did not act on either the free hemiacetal or its sodium salt; if, however, the silver salt of dichlordiethoxyquinone diethylhemiacetal was treated with ethyl iodide, the corresponding tetraethylacetal was formed. As this compound could be obtained only in very small quantities and with great difficulty, it was necessary to prepare the sodium and silver salts of the hemiacetal on a large scale, which was done as follows: 40 grams of dichlordiphenoxyquinone were mixed with the sodic ethylate made by treating 10 grams of metallic sodium with 150 cc. of absolute alcohol, and in order to complete the reaction the mixture was warmed on the steam-bath for a few minutes, and then allowed to stand at ordinary temperatures for four or five hours. The sodium salt of the dichlordiethoxyquinone diethylhemiacetal, which separated in large amount, was fil-

¹ Presented to the American Academy of Arts and Sciences, May 9, 1894.

tered off, and washed thoroughly, first with a mixture consisting of equal parts of alcohol and ether, and finally with ether alone. In this way 40-42 grams of the essentially pure sodium salt were obtained instead of the 44 grams required by the theory; the yield, therefore, was between 90 and 95 per cent. of the theoretical.

In order to prepare the silver salt of the diethylhemiacetal, a concentrated aqueous solution of the sodium salt was treated with 25 grams of argentic nitrate dissolved in a small amount of water. The insoluble silver salt was filtered, washed thoroughly with water, alcohol, and ether, and then dried as quickly as possible by sucking a stream of air through it with the filter-pump.

The silver salt of the dichlordiethoxyquinone diethylhemiacetal was then suspended in ether, and treated in the cold with ethyl iodide, when, in addition to a very small quantity of the tetraethylacetal, a large amount of dichlordiethoxyquinone was obtained. The acetal was separated from the quinone by treating the products of the reaction with a dilute solution of sodic hydrate in 50-per cent. alcohol, which converted the dichlordiethoxyquinone into the sodium salt of chloranilic acid, while the dichlordiethoxyquinone tetraethylacetal was not affected by it. By washing with water it was then easy to separate the freely soluble sodic chloranilate from the insoluble acetal, which was purified by recrystallization from ligroin until it showed the constant melting-point 101° - 102° , when it was dried in a desiccator, and on analysis gave the following results:

I. 0.2039 gram substance gave on combustion 0.3928 gram CO_2 and 0.1335 gram H_2O .

II. 0.2177 gram substance gave on combustion 0.4181 gram CO_2 . The water determination was lost.

III. 0.1843 gram substance gave 0.1304 gram AgCl (Carius).

IV. 0.1620 gram substance gave 0.1135 gram AgCl .

	Calculated for $\text{C}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)_4$.	I.	II.	Found. III.	IV.
Carbon	52.30	52.54	52.37
Hydrogen	7.26	7.28
Chlorine	17.19	17.49	17.32

The yield, as has been already stated, is very small.

Properties of Dichlordiethoxyquinone Tetraethylacetal.—This substance can be obtained from ligroïn in good-sized white rhombic prisms, but when more rapidly crystallized it forms irregularly fan-shaped groups of very much branched needles resembling certain delicate seaweeds, or four-sided plates nearly but not quite rectangular and much striated. It melts at 101° – 102° . By heating in a capillary tube it is apparently not decomposed even at so high a temperature as 275° , but between 260° and 275° it sublimes, giving beautiful white crystals in the upper part of the tube. It is very easily soluble in ether, benzol, alcohol, chloroform, acetone, ligroïn, glacial acetic acid, carbonic disulphide, acetic anhydride, or methyl alcohol, but is insoluble in water. Ligroïn is the best solvent for it.

It is saponified by sulphuric acid of specific gravity 1.44, giving the dichlordiethoxyquinone melting at 104 – 105° , and also a small quantity of chloranilic acid. In the cold the acid produces little or no effect on the acetal, but after warming on the steam-bath for half an hour the saponification is complete. A more dilute acid seems to have no action upon it. Sodid hydrate, even when boiling or mixed with alcohol, does not decompose the acetal.

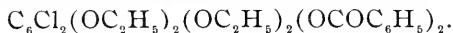
The differences between the properties of the tetraethylacetal and the diethylhemiacetal certainly are remarkable. The hemiacetal is entirely insoluble, while the acetal is exceedingly soluble in all the common solvents except water. The former is very unstable, being readily decomposed by even very dilute acids, while the latter is saponified only slowly by comparatively strong acids when heated with them. By heat also the hemiacetal is easily decomposed, whereas the acetal sublimes apparently unaltered at high temperatures.

The action of bromine on the tetraethylacetal might prove of great interest, as the formation of addition-products from it similar to those obtained by J. U. Nef¹ from quinone, would prove that the four ethoxy groups were attached to the carbonyl radicles of the quinone molecule, and thus settle the constitution of this whole class of compounds. The chances

¹ This Journal, 12, 483.

of the formation of such addition-compounds were, however, small, as Nef has shown² that dichlordiethoxyquinone does not take up bromine, a result which we can confirm; nevertheless we felt that it would be unwise to neglect this experiment. Accordingly one-half gram of bromine dissolved in chloroform was added to one-half gram of the acetal also dissolved in dry chloroform. Even the first drop of the bromine imparted a distinct yellowish-red color to the solution, showing that no bromine addition-compound had been formed. When all the bromine had been added, the solution was allowed to evaporate spontaneously, and although the residue was colored slightly, it was found that the weight had not increased, and after one recrystallization from ligroïn it gave the melting-point of the unaltered acetal, 101°–102°. In another experiment the chloroform-solution was evaporated to dryness on the water-bath, and the same results were obtained. Under no conditions that we have found could the acetal be induced to take up bromine. The negative outcome of these experiments cannot be used in deciding the constitution of the acetal, since its inability to take up bromine is more likely to be due to the presence of the two atoms of chlorine and two ethoxy groups attached to the benzol ring than to the occupation of the double bonds by the four additional ethoxy groups, since dichlordiethoxyquinone does not take up bromine, as has been already stated.

Dichlordiethoxyquinone Dibenzoylethylacetal,



When the diethylhemiacetal itself or its sodium salt was treated with benzoyl chloride at 100° in a sealed tube, no benzoyl compound was formed, but the main products were dichlordiethoxyquinone and ethyl benzoate. A similar result was obtained when the sodium or silver salt of the hemiacetal was suspended in ether, and then treated with benzoyl chloride. When, however, the sodium salt was suspended in alcohol instead of ether and benzoyl chloride added, the dibenzoyl derivative was readily formed, and only a trace of dichlordiethoxyquinone was produced. The following method

² This Journal, 11, 20.

was found to be the best for the preparation of this substance: To 10 grams of the sodium salt of the dichlordiethoxyquinone diethylhemiacetal suspended in a small quantity of alcohol 7.6 grams of benzoyl chloride were added, which gave the proportion of two molecules of benzoyl chloride to one of the sodium salt. There was but little action in the cold, but when the mixture was warmed on the water-bath the reaction took place readily, with the separation of sodic chloride. After cooling, the solution was filtered, and the solid remaining on the filter washed thoroughly with alcohol and water, and then crystallized from hot alcohol until it showed the constant melting-point 170° . The analysis of the substance dried at 100° gave the following results:

I. 0.2428 gram substance gave on combustion 0.5276 gram CO_2 and 0.1230 gram H_2O .

II. 0.2173 gram substance gave 0.1112 gram AgCl (Carius).

	Calculated for $\text{C}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2(\text{OC}_2\text{H}_5\text{OCOC}_6\text{H}_5)_2$.	I.	Found.	II.
Carbon	59.47	59.27	
Hydrogen	5.31	5.63	
Chlorine	12.57		12.65

The yield of the dichlordiethoxyquinone dibenzoyldiethylacetal from 10 grams of the salt is 7.5 grams, or about 66 per cent. of the theoretical yield.

Properties of Dichlordiethoxyquinone Dibenzoyldiethylacetal.—From alcohol it crystallizes in short thick prisms, or, when crystallized more rapidly, in rhombic crystals with a sharp terminal angle, often collected into curving radiated or bladed groups. It is white, and melts at 170° . It is easily soluble in chloroform, carbonic disulphide, ether, or benzol; also in hot ethyl or methyl alcohol, but only slightly soluble in either of these liquids when cold; soluble in warm glacial acetic acid; slightly soluble in hot ligroin; insoluble in water. Sulphuric acid of specific gravity 1.44 saponifies it, forming the compound described in the next section. Sodid hydrate solution, even if boiling or mixed with alcohol, does not decompose it.

The study of the action of reducing agents and of hydroxyl-

amine on the dichlordiethoxyquinone dibenzoyldiethylacetal was of special interest, because it threw so much light upon the constitution of this whole class of substances. If this body were a true acetal, these agents should have no action upon it; if, on the other hand, the ethoxy and benzoyl radicals were not attached to the two carbonyl groups of the quinone molecule, but to the four other atoms of carbon, the substance would be converted into a secondary alcohol by reducing agents, and into an oxime by hydroxylamine.

The reducing agent selected was a mixture of zinc-dust and glacial acetic acid, as this had proved rather the most effective for the conversion of a quinone into a hydroquinone, and there was little or no danger that it would saponify the compound. Even after long continued action there were no signs of reduction, but the unaltered dichlordiethoxyquinone dibenzoyldiethylacetal was recovered from the mixture. This experiment, therefore, goes to prove that the substance is an acetal, and this proof is strengthened by the fact that dichlordiethoxyquinone is converted into the corresponding hydroquinone quickly and easily by this reducing mixture.

To try the action of hydroxylamine 0.2 gram of the dichlordiethoxyquinone dibenzoyldiethylacetal dissolved in alcohol was mixed with an alcoholic solution of one-half gram of hydroxylamine chloride. The solution was boiled over the free flame for half an hour, and then after cooling treated with a large excess of water. The precipitate thus formed after one crystallization from alcohol melted at 170° , and was therefore the unchanged original substance. No other organic substance could be found in the precipitate, or in the aqueous filtrate. The experiment was repeated with an alkaline solution, and again with an acid solution, but in no case could any change in the original acetal be detected. To prove that the indifference of the acetal to the hydroxylamine was not due to the effect of the ethoxy radicals and chlorine atoms attached to its benzol ring, we next studied the action of the chloride of hydroxylamine on dichlordiethoxyquinone. For this purpose one-half gram of it was treated with the chloride of hydroxylamine in alcoholic solution, and the mixture warmed for sixteen hours on the water-bath. Water

precipitated a black substance crystallized in scales, which was thoroughly washed with water to remove all the hydroxylamine salt. It dissolved easily in sodic hydrate, and from this solution acids threw down a reddish gelatinous precipitate. It gave a good test for nitrogen by the potassium method. There can be no doubt, therefore, that the chloride of hydroxylamine acts on dichlorodiethoxyquinone and consequently the indifference of our acetal to this reagent is not due to the presence of the radicles attached to the benzol ring, but is caused by the occupation of the two carbonyl groups by the ethoxy and benzoyl radicles. As we had accomplished our purpose when we had proved that the chloride of hydroxylamine acts on dichlorodiethoxyquinone, we have not tried to study the product more carefully.

Saponification of Dichlorodiethoxyquinone Dibenzo^{yl}diethylacetal.

This substance was boiled with sulphuric acid of specific gravity 1.44, for half an hour in a flask with a return-condenser; a certain amount of gas was given off, and the solid finally went into solution completely, but upon cooling, crystals were deposited, the amount of which was increased by diluting the acid with water. This crystalline precipitate was filtered out, washed repeatedly with water to remove a little chloranilic acid which had been formed in the process, and the residue recrystallized from alcohol until it showed the constant melting-point 142° , when it was dried for analysis. The analysis of this substance gave a great deal of trouble; by using a boat and a stream of oxygen according to the usual method, we were unable to secure complete combustion, and therefore were forced to mix the compound with cupric oxide, and carry on the combustion in an old-fashioned closed tube. This accounts for the fact that our percentages of hydrogen are somewhat high.

I. 0.2119 gram substance gave on combustion, 0.4558 gram CO_2 and 0.0845 gram H_2O .

II. 0.2062 gram gave 0.4452 gram CO_2 and 0.0869 gram H_2O .

III. 0.2020 gram gave 0.4344 gram CO_2 and 0.0830 gram H_2O .

IV. 0.2063 gram gave 0.4451 gram CO_2 and 0.0837 gram H_2O .

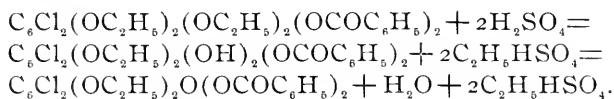
V. 0.1947 gram substance gave 0.1136 gram AgCl (Carius).

VI. 0.2212 gram gave 0.1290 gram AgCl .

	Calculated for $C_{24}H_{20}O_7Cl_2$.	I.	II.	Found.		V.	VI.
Carbon	58.65	58.66	58.88	58.64	58.84
Hydrogen	4.07	4.43	4.67	4.56	4.51
Chlorine	14.46	14.42	14.41

The formula calculated from these analytical results is so strange, that we were at first unwilling to accept it, and thought that perhaps we had the dibenzoate of dichlordiethoxyhydroquinone in our hands, the calculated percentages of hydrogen and chlorine for which agree fairly well with those found by us, whereas the calculated percentage of carbon is over two per cent. higher. This difference we thought might be due to an obstinate impurity, and accordingly we prepared this dibenzoate from dichlordiethoxyhydroquinone, and found that it was entirely different from the saponification-product, as it melts at 215° instead of 142° . The description of this substance is given later in the paper. The supposition that the substance might contain an obstinately adhering impurity was disposed of by frequent recrystallizations. The sample for Analysis I. was crystallized only three or four times, that for II. and III. ten times, that for IV. eight times. There was no difference in the melting-points of these three samples, and, as the results given above show, no essential difference in their percentage composition. We must, therefore, accept the formula derived from these analyses, and the most probable hypothesis is that the atom of oxygen spans the benzol ring between two atoms of carbon in the para position, but we are unable to determine at present whether this atom of oxygen proceeded from the saponification of the ethoxy radicles of the acetal, and therefore lies between the two atoms of carbon to which the benzoate groups are attached, or from the two ethoxy groups of the chloranilic ester, and therefore spans the ring between two other atoms of carbon. This latter supposition seems to us the more probable, as it would give some explanation of the ease with which the ethyls are removed. We wished to confirm such an unusual hypothesis by studying the derivatives of this substance, but our work in this direction has not yet brought any conclusive evidence in regard to its constitution, and we therefore propose this theory only as the most probable one, leaving to future work the testing of its

accuracy. It may be observed here, that such a substance would be a natural product of the saponification of dichlordiethoxyquinone dibenzoyldiethylacetal as shown by the following reactions:



We would call the substance, in accordance with its provisional formula, oxide of dichlordiethoxyquinone dibenzoate, although it may be instead the oxide of dichlorquinone ethylbenzoylacetal.

Properties of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate.—It crystallizes in white well developed six-sided prisms, often of considerable size, belonging either to the hexagonal or to the orthorhombic system. When crystallized more quickly, it forms rather loose rosettes of prisms terminated by several planes forming a very blunt end. It shows a strong tendency to separate from its solutions in the form of a varnish, this result being obtained, for instance, when the alcoholic solution is evaporated to dryness on the water-bath. It melts at 142° , and is readily soluble in alcohol or chloroform; soluble in carbonic disulphide, glacial acetic acid, or benzol; difficultly soluble in ether; insoluble in water. The best solvent for it is alcohol. With aniline it gives two or more products, the study of which next year, we hope, may throw some light on its constitution.

Reduction of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate.

When the substance described in the preceeding paragraph is moistened with a concentrated solution of hydriodic acid, and heated on the water-bath until dry, a reaction takes place, as shown by the separation of free iodine. In order to complete the action the moistening with hydriodic acid and warming was repeated, and the product thus obtained was purified by repeated recrystallization from a very small quantity of alcohol until it showed the constant melting-point 164° , when it was dried at 100° , and analyzed with the following results:

I. 0.2004 gram substance gave on combustion 0.4339 gram CO_2 and 0.0812 gram H_2O .

II. 0.2301 gram substance gave 0.5001 gram CO_2 and 0.0825 gram H_2O .

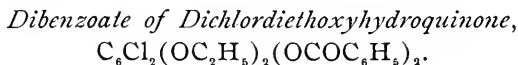
III. 0.2274 gram substance gave 0.1462 gram AgCl (Carius).

IV. 0.1998 gram gave 0.1276 gram AgCl .

V. 0.1990 gram gave 0.1276 gram AgCl .

	Calculated for $\text{C}_6\text{Cl}_2\text{OC}_2\text{H}_5\text{OH}(\text{OCOC}_6\text{H}_5)_2$.		Found.			
	I.	II.	III.	IV.	V.	
Carbon	59.06	59.06	59.28
Hydrogen	3.58	4.50	3.99
Chlorine	15.89	15.90	15.79	15.85

These results agree best with those calculated for the formula given above, although it is not impossible that the substance may contain more hydrogen. It is obvious, however, that the formula of the substance cannot be considered as established, until the analytical data have been supported by experiments with some of its derivatives. We shall not at present indulge in any speculations on the constitution of this substance. It crystallizes usually in balls of indistinct little prisms, but occasionally slender short prisms terminated by a single plane at a very sharp angle were observed. Like its mother-substance, it has a strong tendency to come down from its solutions in the form of a varnish. It melts at 164° , and is very soluble in alcohol, much more so than the oxide from which it was obtained; easily soluble in acetone, or glacial acetic acid; sparingly soluble in ether, benzol, or chloroform; insoluble in carbonic disulphide, or water. It shows weak acid properties, since it dissolves in a solution of sodic hydrate, and is reprecipitated by an acid. Aniline acts upon it, but we have not yet studied the products. Alcohol seems to be the best solvent for it. The study of this substance will be continued in this laboratory next year, and we hope the results of this work will not only definitely establish its formula, but also throw much light on the constitution of the body we have called the oxide of dichlordiethoxyhydroquinone dibenzoate, from which it was obtained.



This substance, which was made in order to compare it with the oxide of dichlordiethoxyhydroquinone dibenzoate just described, was prepared as follows: The sodium salt of the substituted hydroquinone was treated with a slight excess of benzoyl chloride, and the product boiled with water to decompose the benzoyl chloride which had not entered into the reaction. After filtering hot the residue was recrystallized from a mixture of alcohol and chloroform until it showed the constant melting-point 215° , when it was dried at 100° , and analyzed with the following result:

0.2000 gram substance gave 0.1202 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$.	Found.
Chlorine	14.95	14.86

Properties of the Dibenzoate of Dichlordiethoxyhydroquinone.

—It crystallizes from a mixture of alcohol and chloroform in long white prisms terminated by two planes meeting at an obtuse angle; these prisms show a tendency to unite longitudinally. It melts at 215° , and is easily soluble in chloroform; soluble in boiling benzol; sparingly soluble in alcohol even when hot, or in glacial acetic acid; insoluble in ether, carbonic disulphide, ligroin, or water. The dilute acids do not act on it even when boiling, nor does strong hydrochloric acid or strong nitric acid produce any visible effect; strong sulphuric acid also does not act on it in the cold, but when hot dissolves it, forming a slightly dark-colored solution. Alkalies even in strong boiling solution do not decompose it.

Dichlordimethoxyquinone Dibenzoyldimethylacetal.



This substance was made in the hope that its saponification might throw some additional light on the curious products obtained from the corresponding ethyl compound, and described in the preceding sections. For this purpose 17 grams of the sodium salt of dichlordimethoxyquinone dimethylhemiacetal were suspended in methyl alcohol, and 20 grams of benzoyl chloride added (this is a little more than the calculated amount), after warming for a short time to finish the reaction, the liquid was allowed to cool, the solid, which had

separated, filtered out, and washed first with alcohol and afterward with water. The residue was purified by crystallization from a mixture of alcohol and chloroform until it showed the constant melting-point 193° , when it was dried at 100° , and analyzed with the following result:

0.2052 gram substance gave 0.1163 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$.	Found.
Chlorine	13.95	14.02

The substance crystallizes from a mixture of alcohol and chloroform in several different forms, which, however, may be produced by the twinning of a single form in different ways. The simplest form observed consisted of rather long plates terminated by two planes at an obtuse angle to each other; these frequently appeared as broad plates in radiating groups, when less well developed. A second very common form was white thick plates, square or nearly so, which showed evidence of twinning, and finally mixed with these were sharp thick rhombic crystals looking like very acute scalenohedra, and showing a line of twinning along the diagonal between the two acute angles. Whether these were different habits of the same form, or indicated that the substance was not homogeneous mattered little to us, as the saponification with sulphuric acid of specific gravity 1.44 gave a product which was evidently homogeneous, and this was the substance in which we were especially interested. The dichlordimethoxyquinone dibenzoyldimethylacetal is white, and melts at 193° . It is easily soluble in chloroform; soluble in benzol; sparingly soluble in alcohol, ether, glacial acetic acid, or carbonic disulphide; insoluble in water or ligroin. The best solvent for it is a mixture of alcohol and chloroform.

Saponification of Dichlordimethoxyquinone Dibenzoyldimethylacetal.

The substance was boiled with sulphuric acid of specific gravity 1.44, in the manner already described under the corresponding ethyl compound, and the phenomena observed in this case were exactly similar to those presented by the ethyl compound. The product of the reaction was purified by recrystallization from a mixture of chloroform and alcohol until

it showed the constant melting-point 205° – 206° , when it was dried at 100° , and analyzed with the following result :

0.2071 gram substance gave 0.1288 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$.	Found.
Chlorine	15.33	15.38

This product therefore corresponds to that obtained by the saponification of the ethyl compound, and this view of its nature is confirmed by the striking similarity between these two substances in crystalline form.

Properties of the Oxide of Dichlordimethoxyhydroquinone Dibenzoate.—It crystallizes from a mixture of alcohol and chloroform in white well formed rhombic prisms, shorter than they are broad, terminated by a very obtuse octahedron and a basal plane forming a very blunt end ; the prisms are frequently rendered six-sided by the presence of two basal planes on the acute edges. It melts at 205° – 206° , and is readily soluble in chloroform ; soluble in glacial acetic acid, or benzol ; slightly soluble in alcohol, acetone, or carbonic disulphide ; very sparingly soluble in ether ; insoluble in water. The best solvent for it is a mixture of alcohol and chloroform.

Dichlordiethoxyquinone Diethylacetaldicarbonic Ester,
 $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2$.

After we had succeeded in replacing the sodium in the salts of the hemiacetals described in this paper with the benzoyl radicle, it seemed of interest to see whether other acid chlorides would act in the same way, and we therefore tried the action of chlorocarbonic ester. Four grams of the sodium salt of dichlordiethoxyquinone diethylhemiacetal suspended in absolute alcohol were mixed with a slight excess of chlorocarbonic ester, and warmed on the steam-bath for a few minutes in order to complete the reaction. The solution was filtered while still hot from the precipitate of sodic chloride, and the filtrate on cooling deposited well formed crystals of the new substance, which was purified by recrystallization from alcohol until it showed the constant melting-point 122° – 123° , when it was dried, and analyzed with the following result :

0.1866 gram substance gave 0.1075 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2$.	Found.
Chlorine	14.18	14.24

The substance crystallizes in white flat prisms, terminated usually by a single plane at a very sharp angle, which is occasionally modified by a second smaller plane. It melts at 122° – 123° , and is readily soluble in alcohol, chloroform, benzol, or acetone; soluble in glacial acetic acid or carbonic disulphide; slightly soluble in ether; insoluble in water. The best solvent for it is alcohol. In view of the results of the saponification of the corresponding benzoyl compound the decomposition of this substance with sulphuric acid of specific gravity 1.44 promises to be interesting. Unfortunately, it was prepared just before the vacation, so that this work must be postponed until the next college year.

*Action of Potassic Phenylate on Dichlordiphenoxyquinone—
Tetraphenoxyquinone, $C_6(OC_6H_5)_4O_2$.*

By treating 10 grams of pure dichlordiphenoxyquinone with a little more than two equivalents of potassic phenylate, made by dissolving 4 grams of potassic hydrate and 12 grams of phenol in 150 cc. of water, tetraphenoxyquinone was formed. In order to complete the reaction it was necessary to boil the dichlordiphenoxyquinone with the potassic phenylate for twenty to thirty minutes. The product formed was then filtered off, and after washing thoroughly with water and alcohol was purified by crystallization from benzol until it gave the constant melting-point of 229° – 230° . After drying at 100° , the substance gave the following results on analysis:

I. 0.2198 gram substance gave on combustion 0.6122 gram CO_2 and 0.0865 gram H_2O .

	Calculated for $C_6(OC_6H_5)_4O_2$.	Found.
Carbon	75.63	75.97
Hydrogen	4.20	4.37

This body can also be formed by the action of four equivalents of potassic phenylate in aqueous solution on chloranil, or by the action of sodic phenylate on the dichlordiphenoxyquinone suspended in benzol. In this latter case the sodic phenylate was prepared by dissolving phenol in a rather large

volume of benzol, and then adding the required quantity of sodium, which disappeared completely after warming the solution on the steam-bath for some time. Neither of these methods gives so good a result as the one described at the beginning of this section. On the other hand, the tetraphenoxiquinone is not formed when the dichlordiphenoxiquinone is treated with sodic phenylate, which has been made by the action of metallic sodium on absolute alcohol mixed with phenol, as in this case the principal product is diethoxydiphenoxiquinone.

Properties of Tetraphenoxiquinone.—It crystallizes from benzol in red prisms which, when well developed, have blunt ends formed by a number of planes or by a single plane at an oblique angle. When smaller they appear as long somewhat shuttle-shaped prisms, radiating from a common centre, but not forming circular groups. It melts at 229° – 230° , and is soluble in hot chloroform, boiling acetic anhydride, or boiling benzol; slightly soluble in carbonic disulphide, or boiling glacial acetic acid; very sparingly in warm acetone; insoluble in water, alcohol, ether, or ligroin. The best solvent for it is boiling benzol.

The tetraphenoxiquinone is not easily attacked by reducing agents: sulphurous acid at ordinary temperatures, or in a sealed tube at 100° , has no action on it; hydriodic acid, or a mixture of stannous chloride and hydrochloric acid, reduces it, but the action is very slow; on the other hand, it is easily reduced by glacial acetic acid and zinc-dust.

Saponification of Tetraphenoxiquinone.

Toward acid saponifying agents the tetraphenoxiquinone shows a remarkable stability. Sulphuric acid of specific gravity 1.44 has no effect whatever, even after long continued boiling, but hot strong sulphuric acid of specific gravity 1.83 dissolves it, giving a solution from which nothing is precipitated on adding water. This may be due to the formation of a sulphonic acid, but we have not as yet studied the reaction carefully.

A better result was obtained by boiling the tetraphenoxiquinone with a solution of sodic hydrate (one part in four)

for about two hours, as it was then completely dissolved, giving a dark purple color to the solution, which on cooling deposited small black crystals of a sodium salt. The alkaline solution, when poured into an excess of dilute acid, gave a reddish-yellow precipitate, which was filtered out, washed with water, and, after purification by recrystallization from alcohol, dried, and analyzed with the following result:

0.2224 gram substance gave on combustion 0.5436 gram CO_2 and 0.0794 gram H_2O .

	Calculated for $\text{C}_6(\text{OC}_6\text{H}_5)_2(\text{OH})_2\text{O}_2$.	Found.
Carbon	66.68	66.65
Hydrogen	3.70	3.97

The substance was therefore formed from the tetraphenoxyquinone by replacing two of the phenyl radicles by hydrogen, and is the diphenoxyanilic acid.

Properties of Diphenoxyanilic Acid, $\text{C}_6(\text{OC}_6\text{H}_5)_2(\text{OH})_2\text{O}_2$.—It forms glistening, rather thick plates, either square or in rectangular oblong forms, having a dark reddish-brown color like that of ferric citrate, which the substance also resembles in lustre and general appearance. It melts at about 276° , but the melting-point is not sharp, as it shows signs of softening even at 270° . If heated somewhat above its melting-point, it puffs up, filling the capillary tube with a dark liquid. It is soluble in glacial acetic acid; sparingly soluble in alcohol or hot chloroform; insoluble in ether, benzol, carbonic disulphide, or ligroin. It dissolves slightly in boiling water, imparting a pink color to the solution. It has distinct acid properties, dissolving in sodic hydrate to form a black crystalline salt, which dissolves in water with a dark purple color. It is not acted on by acids dilute or strong, cold or hot.

Tetraphenoxyhydroquinone, $\text{C}_6(\text{OC}_6\text{H}_5)_4(\text{OH})_2$.

This body was made by reducing the tetraphenoxyquinone with glacial acetic acid and zinc-dust. Two grams of the tetraphenoxyquinone were warmed on the steam-bath with these reagents until the red color of the original substance had completely disappeared; water was then added, and the precipitated hydroquinone purified by recrystallizing it from alcohol containing a little hydriodic acid to prevent oxidation. On analysis the following results were obtained:

0.2015 gram substance gave on combustion 0.5558 gram CO_2 and 0.0862 gram H_2O .

	Calculated for $\text{C}_6(\text{OC}_6\text{H}_5)_4(\text{OH})_2$.	Found.
Carbon	75.32	75.21
Hydrogen	4.60	4.75

Properties of the Tetraphenoxyhydroquinone.—It crystallizes from alcohol in white, well developed, rather thick rhombic plates, with a very acute angle, which sometimes show sharp notches in the two ends. When seen on the edge the plates seem to be monoclinic, and are often twined on the basal plane. Larger crystals are apt to have the form of sharp spear-heads. At 210° it shows signs of decomposition by beginning to turn red. This change of color increases as the temperature rises, until finally it melts at 219° – 220° , giving a light red liquid, which on cooling solidifies to a red body, probably the quinone. It is readily soluble in acetone; somewhat more sparingly soluble in ethyl alcohol, methyl alcohol, or chloroform; sparingly soluble in cold glacial acetic acid, more readily in hot; very sparingly soluble in benzol or ether. It is insoluble in water, carbonic disulphide, or ligroin. Alcohol is the best solvent for it.

Diethoxydiphenoxyquinone, $\text{C}_6(\text{OC}_2\text{H}_5)_2(\text{OC}_6\text{H}_5)_2\text{O}_2$.

This substance was obtained in some of our earlier attempts to make tetraphenoxyquinone by treating dichlordiphenoxyquinone with sodic phenylate dissolved in absolute alcohol. 10 grams of dichlordiphenoxyquinone were mixed with two equivalents of sodic phenylate made by treating 1.6 grams of sodium with about 20 cc. of absolute alcohol and then adding 8 grams of phenol. On the addition of the sodic phenylate the dichlordiphenoxyquinone became dark-colored, and a very black, tarry solution was obtained, which, after standing for two hours, was separated by filtration from the sodic chloride formed; water was then added to the filtrate, which precipitated an oily black liquid. In order to purify this liquid it was repeatedly washed with water by decantation, and then dissolved in alcohol, from which beautiful silky orange-yellow needles were obtained, and these were recrystallized from alcohol until they showed the constant melting-

point 128° , when after drying in a desiccator they gave the following results on analysis :

0.2104 gram substance gave on combustion 0.5324 gram CO_2 and 0.1004 gram H_2O .

	Calculated for $\text{C}_6(\text{OC}_2\text{H}_5)_2(\text{OC}_6\text{H}_5)_2\text{O}_2$.	Found.
Carbon	69.47	69.01
Hydrogen	5.26	5.30

The yield is small. The diethoxydiphenoxyquinone crystallizes in long silky orange-yellow slender needles arranged in radiating groups. It melts at 128° , and is readily soluble in alcohol or chloroform; soluble in carbonic disulphide or benzol; sparingly soluble in ether or glacial acetic acid; insoluble in ligroin or water. The best solvent for it is alcohol.

Action of Sodid Methylate on Tetraphenoxxyquinone—Dimethoxydiphenoxxyquinone, $\text{C}_6(\text{OCH}_3)_2(\text{OC}_6\text{H}_5)_2\text{O}_2$.

When 5 grams of tetraphenoxxyquinone were treated with a solution of 6 equivalents of sodid methylate in methyl alcohol, they dissolve to a colorless liquid, which on standing deposited a quantity of nearly white needles. These were filtered off, and, after washing with a little methyl alcohol, treated with water rendered alkaline by sodid hydrate, when a portion of the substance was dissolved, and a yellow crystalline body was left as an insoluble residue. This latter substance was purified by crystallization from a mixture of benzol and alcohol until it showed the constant melting-point of 171° , when it was dried at 100° , and analyzed with the following result :

0.2043 gram substance gave on combustion 0.5068 gram CO_2 and 0.0862 gram H_2O .

	Calculated for $\text{C}_6(\text{OCH}_3)_2(\text{OC}_6\text{H}_5)_2\text{O}_2$.	Found.
Carbon	68.19	67.66
Hydrogen	4.55	4.69

The substance is therefore dimethoxydiphenoxxyquinone formed by the replacement of two of the phenyl by methyl radicles.

Properties of Dimethoxydiphenoxxyquinone.—It crystallizes from a mixture of alcohol and benzol in beautiful long golden-yellow needles, which under the microscope are seen to be

slender prisms arranged in radiating groups. The terminations of these prisms consist of one principal plane, sometimes at a right angle, sometimes at an oblique angle to the sides; in this latter case, when the crystals are large enough, small modifying planes are also seen. It melts at 171° , and is readily soluble in chloroform; soluble in ethyl or methyl alcohol, benzol, or glacial acetic acid; sparingly soluble in ether or carbonic disulphide: insoluble in ligroin or water. It is reduced by zinc and glacial acetic acid to a colorless hydroquinone.

It dissolves apparently with decomposition in a dilute solution of sodic hydrate, and from this solution dilute sulphuric acid precipitates a non-crystalline body insoluble in water, but soluble in sodic hydrate with a fine purple color. We have not had time as yet to study this substance more carefully.

When the yellow dimethoxydiphenoxyquinone was mixed with a solution of sodic methyrate in methyl alcohol, and the mixture stirred vigorously, the yellow solid disappeared, and a white crystalline sodium salt was precipitated. This precipitate dissolved in water without residue, and from the solution the addition of a dilute acid threw down a white amorphous solid, which decomposed almost immediately into a yellow substance, probably dimethoxydiphenoxyquinone. These observations show that in this case a hemiacetal was formed, but a much less stable one than that obtained from the quinones containing chlorine. It seems, therefore, that the stability of the hemiacetals depends on the number and strength of the negative radicles attached to the quinone ring.

Action of Sodid Phenylate on Bromanil.

In order to study this action 2 grams of bromanil, prepared according to Stenhouse,¹ were treated with an alcoholic solution² of sodic phenylate made by acting on 0.3 gram of sodium with absolute alcohol and then adding 3 grams of phenol. The bromanil began to turn red as soon as the phenylate was added, but it was necessary to warm the mixture in order to

¹Ann. Chem. (Liebig) Suppl. 8, 13.

²This experiment was tried early in our work, before we had found that an aqueous solution of the sodic phenylate acted better on chloranil than the same reagent dissolved in alcohol. If we were to repeat this preparation, therefore, we should use a solution in water instead of in alcohol.

make the reaction complete. After this the solution was filtered, and the solid remaining on the filter, after thorough washing with water and alcohol, was purified by crystallization from benzol until it showed the constant melting-point 266° – 267° , when it was dried at 100° and analyzed with the following result :

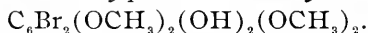
0.1677 gram substance gave 0.1393 gram AgBr (Carius).

	Calculated for $C_6Br_2(OC_6H_5)_2O_2$.	Found.
Bromine	35.56	35.36

The substance is, therefore, dibromdiphenoxyquinone, and it is to be observed that bromanil behaves differently from chloranil with this alcoholic solution of sodic phenylate, for the latter lost all four of its atoms of chlorine, two being replaced by phenoxy and two by ethoxy groups. The bromanil, on the other hand, behaves with the alcoholic solution of sodic phenylate as chloranil does with an aqueous solution of this reagent, the action consisting in the replacement of two atoms of halogen by two phenoxy groups.

Properties of Dibromdiphenoxyquinone.—It crystallizes from benzol in rather short orange-red needles with blunt points, melting at 266° – 267° . It is very slightly soluble in alcohol even when hot; insoluble in ether or ligroin, or in water whether cold or hot; sparingly soluble in carbonic disulphide or boiling benzol, and only very slightly soluble in cold benzol; more soluble in chloroform; freely soluble in hot glacial acetic acid, slightly in cold. The three strong acids have no visible effect upon it. By the action of glacial acetic acid and zinc-dust it is reduced to a colorless hydroquinone. It reacts easily with sodic methylate, ethylate, or phenylate, and also with sodium malonic ester, or aniline, but we have studied only its action with sodic methylate.

Dibromdimethoxyquinone Dimethylhemiacetal,



This body was formed by treating 1.4 grams of dibromdiphenoxyquinone with a solution of rather less than four equivalents of sodic methylate in methyl alcohol, which was made by the action of a little methyl alcohol on 0.3 gram of metallic sodium. When the sodic methylate was first added,

there was no apparent action, but after warming on the steam-bath for a few minutes a white crystalline sodium salt separated. The salt was filtered out, washed with a little methyl alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results:

0.2047 gram substance gave 0.1966 gram AgBr (Carius).

	Calculated for $C_6Br_2(OCH_3)_2(OH)_2(OCH_3)_2$.	Found.
Bromine	41.03	40.88

The dibromdimethoxyquinone dimethylhemiacetal is a white amorphous solid insoluble in all the common solvents. It melts at 178° – 188° , at the same time changing to a red substance, probably dibromdimethoxyquinone. The change can also be produced by treatment with dilute sulphuric acid, or dilute hydrochloric acid. From this description of the preparation and properties of this hemiacetal it is evident that the action of sodic methylate on dibromdiphenoxyquinone is similar in every respect to the action of this reagent on the corresponding compound containing chlorine.

Action of Potassic Phenylate on Trichlorquinone.

By treating 5 grams of trichlorquinone suspended in water with 2 equivalents of potassic phenylate, made from 2.7 grams of potassic hydrate and 8 grams of phenol, a semi-liquid substance was formed. After the mixture had been heated on the steam-bath for twenty minutes in order to complete the reaction, the supernatant liquid was poured off, and the pasty residue washed with water by decantation, and then warmed with alcohol, which converted it into a crystalline solid. These crystals were then separated by filtration, washed thoroughly with cold alcohol, and recrystallized from alcohol containing a small amount of benzol until they showed the constant melting-point 169° – 170° , when they were dried at 100° , and analyzed with the following results:

I. 0.1888 gram substance gave 0.0818 gram AgCl (Carius).

II. 0.1913 gram substance gave 0.0832 gram AgCl.

	Calculated for $C_6HCl(OC_6H_5)_2O_2$.	I.	Found. II.
Chlorine	10.87	10.71	10.75

Properties of Monochlordiphenoxyquinone.—It crystallizes from alcohol in long, slender, pointed oval plates arranged in irregular groups,—a very characteristic habit of crystallization. It has an orange color, with a slight brownish tinge, and melts at 169° – 170° . It is easily soluble in benzol or chloroform; difficultly soluble in alcohol; slightly soluble in carbonic disulphide; insoluble in water, ether, or ligroin. It is easily reduced to a colorless hydroquinone by glacial acetic acid and zinc-dust.

To see whether it would form a hemiacetal, 0.5 gram of the monochlordiphenoxyquinone was treated with the sodic methylate made by acting on 0.3 gram of metallic sodium with a few cc. of methyl alcohol. The quinone dissolved in the cold, but, even when allowed to stand for some time and stirred vigorously, no precipitate of a sodium salt was formed. When, however, it was warmed for a few minutes, a heavy white precipitate was deposited, which, after being washed with a little methyl alcohol, dissolved completely in water, giving a clear solution. The addition of an acid to this solution produced a turbidity, which soon developed into a white precipitate, undoubtedly the hemiacetal, but this passes so easily into a red quinone-derivative that we have not attempted to analyze it, especially as its properties leave no doubt as to its nature. It follows from these observations that the stability of the hemiacetals is increased by the number of negative radicles, such as chlorine atoms, present.

Action of Sodic Ethylate on Quinone.

Although the results described in the last section made it probable that the hemiacetal derived from quinone itself would be very unstable, we have tried some experiments on the action of sodic ethylate on quinone ($C_6H_4O_2$), and think it best to give a preliminary account of them here, in spite of the fact that they have not led as yet to any definite result. They have, however, proved that sodic ethylate acts on quinone, but have by no means convinced us that the product is a hemiacetal. On treating quinone dissolved in ether with

an alcoholic solution of sodic ethylate, a heavy, flocculent, dark-green precipitate is formed, which is insoluble in ether, but dissolves in alcohol or water with decomposition. This precipitate does not seem to be homogeneous, as by fractional precipitation products were obtained unlike in color, and also in their composition, as shown by analysis; moreover its study is rendered difficult by the fact that it takes fire spontaneously when dried at ordinary temperatures in the air; if, however, it is dried in an atmosphere of hydrogen, it can be exposed to the air without taking fire at ordinary temperatures, but, if warmed to 40° , it begins to glow, and burns like tinder. Before studying this rather unmanageable substance further, we tried to get some idea of the way in which the reaction ran by a quantitative study of it, based upon the fact that all the quinone can be removed from its ethereal solution by the sodic ethylate.

In the first trial it was found that 1 gram of quinone required 0.2352 gram of sodium for complete precipitation.

In the second trial 1 gram of quinone required 0.2460 gram of sodium.

In the third trial, 3 grams of quinone required 0.6 gram of sodium.

These results indicate that each molecule of quinone acts with only 1 molecule of sodic ethylate, as the amount of sodium needed in this case for 1 gram of quinone is 0.213 gram, and the observed results come as near to this number as could be expected, when the roughness of the method is considered. This conclusion is confirmed by the yield of the salt obtained from 3 grams of quinone, which was 4.7 grams, whereas, if only 1 molecule of sodic ethylate had been added to each molecule of the quinone, the yield should have been 4.9 grams. The study of other parts of this research has occupied our time so completely that we have been unable to do more on this division of the subject, but we hope that this work can be taken up again in this laboratory at an early date.

Experiments on Phenoquinone.

It has been suggested in the introduction that phenoqui-

none and quinhydrone may be hemiacetals similar to those studied in this paper. In that case phenoquinone should contain two hydroxyl groups, and form salts. Accordingly, we have tried to obtain a salt of it, although the chances of success were not great, as Wichelhaus¹ has stated that phenoquinone forms no salts, but is decomposed by alkalies. Still we thought that possibly by using sodic ethylate in insufficient quantity we might succeed, as the replacement of the hydrogen by the metal might take place in preference to the decomposition of the phenoquinone, especially as Wichelhaus also states that it gives a blue color with alkalies. We proceeded as follows: One gram of phenoquinone² was dissolved in ether, and treated with an alcoholic solution of the sodic ethylate made from 0.1 gram of sodium; as 0.154 gram of sodium would be required for two atoms of sodium to each molecule of phenoquinone, there was a considerable excess of this latter substance. As soon as the sodic ethylate was added, a heavy, flocculent, dark-green precipitate was formed, which was filtered out, washed thoroughly with ether, and dried over sulphuric acid and paraffine. We hoped at first that this was the salt of phenoquinone, and three sodium determinations seemed to confirm this idea, as they gave 13.14, 13.41, and 14.31 per cent. of sodium, which is not far from the number calculated for a sodium salt of phenoquinone, since that is 13.52 per cent. of sodium; but the study of the ethereal filtrate from the salt threw a great deal of doubt on this conclusion, since it contained a large amount of phenol. We think it more probable, therefore, that the sodic ethylate decomposed the phenoquinone into quinone and phenol, and that the green salt was then formed by the action of the sodic ethylate upon the quinone, the action being the same as that described in the last section. This inference is strengthened by the marked resemblance in appearance between the salts obtained in these two cases, and also by the study of the

¹ Ber. d. chem. Ges., 5, 248.

² The phenoquinone was made by adding 1 equivalent of quinone dissolved in hot ligroin to 2 equivalents of phenol dissolved in a small quantity of the same solvent. The mixed solutions were warmed for a few minutes, and then on cooling beautiful red crystals separated, which were purified by recrystallization from alcohol.

properties of the salt made from the phenoquinone, since it dissolved completely in water, forming a dirty-green solution, and undoubtedly suffering partial decomposition, as ether extracted from this solution colorless crystals of hydroquinone recognized by their melting-point of 169° . The addition of an acid to this solution gave no precipitate, and upon shaking out the acidified liquor with ether, nothing was extracted but hydroquinone. If the substance had been the desired salt of phenoquinone, phenol should have been obtained from this filtrate. Although these experiments tell against the formation of salts of phenoquinone, we do not consider them absolutely final, but the study of the action of alkalis on phenoquinone under other conditions will be continued in this laboratory during the coming college year.

As we had not succeeded in making a salt of phenoquinone we next turned our attention to the action of sodic phenylate on quinone, as, if the phenoquinone is a hemiacetal, this should act as well as free phenol, whereas, according to the other theories of the constitution of phenoquinone, it is hard to see how there should be any action in this case. Sodic phenylate was made by warming the proper amount of metallic sodium with a solution of phenol in benzol until the sodium had entirely disappeared. As the benzol cooled, the white crystalline sodic phenylate separated abundantly, and, after filtering, any free phenol was removed by washing with cold benzol. Upon adding the solid sodic phenylate to a solution of quinone in absolute ether a dark red crystalline substance looking like phenoquinone was formed. After evaporating off the ether slowly, the residue dissolved easily in water with a slight green color, and acids precipitated from this aqueous solution a small amount of a dark reddish solid. The ethereal solution showed a tendency to turn green round the edges during the evaporation which may perhaps have been due to the action of the moisture in the air. If benzol was used to dissolve the quinone instead of ether, a pink substance was formed, which changes to a dark-green body when warmed. With ligroïn as the solvent, a dark-green precipitate was obtained at first. Unfortunately, this work was undertaken at the very end of the term, so that a more careful study of these

products must be postponed until next year, but these preliminary experiments show that sodic phenylate does combine with quinone, and therefore lend a certain amount of countenance to our suggestion that phenoquinone is a hemiacetal.

Contributions from the Chemical Laboratory of Cornell University.

PARANTHRACENE OR DIANTHRACENE: A POLYMERIC MODIFICATION OF ANTHRACENE.

BY W. R. ORNDORFF AND F. K. CAMERON.

The remarkable change which anthracene (or photene) undergoes when its solution in alcohol or benzene is subjected to the direct action of the sun's rays, was first observed in 1866 by J. Fritzsche,¹ who gave the name paraphotene to the product formed. A little later Graebe and Liebermann² also noticed this peculiar transformation of anthracene, but they called the compound which separates out of the solutions "paranthracene," as they had previously shown that Fritzsche's photene was identical with the anthracene of Laurent and Anderson. This substance was characterized by its insolubility in all the usual solvents, its indifference to both nitric acid and bromine and the fact that at its melting-point, 244°, it is changed into anthracene melting at 213°.

In 1874 E. Schmidt³ investigated paranthracene with the idea of obtaining from it nitro derivatives of anthracene, as it resisted the action of reagents and appeared to be more stable than anthracene itself. He confirms the statement of the previous investigators in regard to its insolubility, its reversion into anthracene at its melting-point (244°-245°), and the fact that it is not acted upon by bromine or nitric acid. With picric acid it forms no compound as anthracene does, and when it is acted upon by the strongest reagents it gives, according to Schmidt, substitution-products of anthracene, being apparently first converted into that hydrocarbon.

No further work appears to have been done on paranthracene till 1891, when K. Elbs⁴ attempted to determine the mole-

¹J. prakt. Chem. **101**, 337; **106**, 274; Ztschr. Chem. 1867, 290.

²Ann. Chem. (Liebig) Suppl. **7**, 264 (1870).

³J. prakt. Chem. [2] **9**, 247.

⁴*Ibid.*, [2] **44**, 467.

cular weight of the substance by the freezing-point method. The product with which Elbs worked is described as melting not quite sharply at 272° – 274° , and the statement is made that it remained unchanged when heated alone to 260° or when its solution in dimethylaniline was boiled, though it was partially converted into anthracene when heated in naphthalene to the boiling-point of that substance (218°) and completely when warmed to 260° in diphenylamine. Elbs found that paranthracene exhibited no fluorescence either in solution or in the solid form, and was extraordinarily insoluble in the usual solvents. In naphthalene, the material selected by Elbs for the molecular-weight determinations, it dissolves to the extent of only 0.229 parts in 100 of the solvent at the melting-point, so that the depressions of the freezing-point measured are necessarily very small. To eliminate experimental errors as much as possible, it was found necessary therefore to estimate the melting-point of the pure naphthalene as well as that of the solution, as the mean of a series of determinations. "In dieser Weise," he continues, "ergab sich aus 10 Reihen mit im Ganzen 118 Einzelablesungen als mittleres Molekulargewicht des Paranthracens die Zahl 303, wobei der niedrigste beobachtete Werth 248, der höchste 344 war; bestehend eine zusammengehörige Gruppe von Messungen, ausgeführt mit einem einfachen Beckmann'schen Apparat, dessen Thermometer in $\frac{1}{50}^{\circ}$ eingetheilt ist :

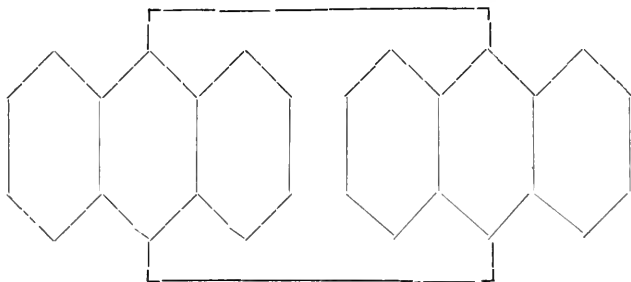
Procentgehalt der Lösung.	Depression.	Molecular- gewicht.	Anzahl der Versuche.
0.059	0.012°	344	7
0.108	0.023	329	7
0.132	0.027	342	7
0.146	0.037	276	8
0.229	0.053	303	10 "

From these results Elbs concludes that paranthracene is formed from anthracene by the combination of two molecules of the latter. He found it impossible to make derivatives of paranthracene by the action of any reagent. The products he obtained were either indefinite or derivatives of anthracene itself. When treated with bromine in the sunlight both anthracene and paranthracene gave the same product, dibromanthracene tetrabromide.

In regard to the relation between anthracene and paranthracene he says nothing further.

The most recent work on paranthracene is that of Linebarger,¹ who made the substance by exposing anthracene to the sunlight in benzene, toluene, xylene, ethylbenzene, alcohol, acetic acid, ethyl benzoate, benzene bromide, chloroform, ethylene bromide, and carbon bisulphide. The melting-point of the material obtained from all the above liquids except ethylene bromide and carbon bisulphide varied from 243° to 245 , the low melting-points of the material from ethylene bromide (210° – 212°) and carbon bisulphide (207° – 211°) being due, according to Linebarger, to the fact that these solvents are themselves decomposed by light and the substance was contaminated with the decomposition-products of the solvents. As to the way in which the two molecules of anthracene combine to form one molecule of paranthracene, Linebarger offers the following hypothesis, basing his conclusions on the work of Elbs: "It is pretty well established that in anthracene the so-called γ -carbon atoms have one bond in common, *i. e.*, anthracene may be regarded as ethane in which four of the hydrogen atoms are replaced by two bivalent radicles, *viz.*, phenylene; or what amounts to the same thing, anthracene consists of *three benzene rings*, of which the middle one has two of its carbon atoms, in the para position bound directly together. This double (?) linkage of the γ -carbon is quite loose, as shown by the ready oxidation of anthracene into anthraquinone, and the formation of addition-products with chlorine and bromine at low temperatures. It might be now, that by the action of the sun's rays these double (?) bonds would be set free in some way. If, then, a molecule of anthracene with its double (?) bonds thus loosened should come within the sphere of action of another molecule in a similar condition, the free bonds of the one molecule might unite with the free bonds of the other, doubling up and forming a new molecule, stable so far as the action of the light is concerned. In direct sunlight, the equilibrium of the anthracene molecule is *labile*, while that of the paranthracene is *stable*. On the other hand, under the influence of heat the

paranthracene is in labile, and the anthracene in stable equilibrium, for at 244° the double molecule decomposes into two simple ones—paranthracene changes into anthracene. There is then in paranthracene a *ring of four carbon atoms*, occupying with respect to the anthracene molecule the γ -position." In the *Jahrbuch der Chemie* for 1893 (p. 147), this idea of Linebarger's is given expression in the following formula :



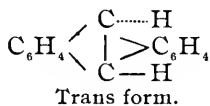
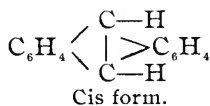
It will be seen from this review of the subject that the exact relation between anthracene and paranthracene is not yet determined. No analyses of paranthracene have been made, or at least if made they have not yet been published, so that it is by no means certain that anthracene and paranthracene have the same percentage composition. All previous investigators seem to have been satisfied that anthracene and paranthracene had the same percentage composition because anthracene changed into paranthracene in the sunlight, and on heating paranthracene to its melting-point (244°), it gave a product which, after solidification, melted at 213° , the melting-point of anthracene.

It will be seen too that the determinations of the molecular weight of paranthracene made by Elbs are far from satisfactory. Owing to the slight solubility of the material in naphthalene at its point of solidification the depressions measured by the thermometer graduated *in fiftieths of a degree* were only 0.012 — 0.053° . This fact makes a very small experimental error of great importance in the molecular-weight column. For example, a difference of 0.01° in the readings will frequently change the result from the double to the single molecule. In addition to this the fact that the paranthra-

cene with which Elbs worked melted at 272° – 274° , while all the other investigators give the melting-point as about 244° , would seem to indicate that his material was impure.

In his molecular-weight determinations it will be noted that in one case Elbs worked up to the limit of solubility of paranthracene in naphthalene which might vitiate these results on account of the possibility of some of the dissolved material separating out when the temperature of the solvent is lowered to determine the freezing-point. Besides this it is well-known that it is no easy matter to make molecular-weight determinations by the freezing-point method in such a high melting and volatile substance as naphthalene. Moreover, these results of Elbs have never been confirmed by any other chemist nor have like results been obtained with any other solvent than naphthalene, so that the molecular weight of paranthracene may be still regarded as doubtful.

Furthermore, from a comparison of the physical properties of anthracene and paranthracene, and the fact that each may be readily transformed into the other and that both give the same products when acted on by the same reagents, it will be seen that these two substances bear to each other much the same relation as that frequently observed between two stereoisomers. If now the space-formula for anthracene be examined it will be found that it admits of two configurations, the one corresponding to the *cis*, the other to the *trans* form, as shown in the following formulas, in which the dotted line represents the hydrogen atom below the plane of the paper, and the unbroken line that above :



It seemed highly desirable, therefore, that further and more careful work should be done before any speculations as to the structural formula of paranthracene and its relations to anthracene were indulged in. Pure paranthracene was therefore made, analyzed, and its properties and crystal form carefully studied. The molecular weight of the pure substance was then determined by the boiling-point method, which has

the great advantage over the freezing-point method, in that paranthracene is very much more soluble in liquids at their boiling-points than at their freezing-points, consequently the rise in the boiling-point is much greater than the depression of the freezing-point, so that errors of observation do not affect the final results to anything like the same degree. Regarding certain other advantages that the boiling-point method of determining molecular weights has over the freezing-point method the reader is referred to a recent communication by us.¹

EXPERIMENTAL.

The paranthracene was made by exposing purified anthracene suspended in benzene and xylene in thin white glass bottles, to the direct action of the sunlight for some weeks during the Summer and Fall of the year 1894. The bottles were shaken from time to time to remove as soon as possible the materials from the sides and to dissolve the anthracene remaining unacted upon at the bottom of the bottles. By this means the action of the sunlight was not prevented by the opaque material adhering to the sides of the bottles and the conversion of the anthracene into paranthracene was completed in a much shorter time. When paranthracene no longer separated out the solid material was filtered from the liquids, which were generally colored reddish yellow, washed with benzene and dried. This crude material was boiled in a flask connected with a reflux condenser, first with alcohol, then with acetic ether and finally with benzene, in order to remove substances soluble in these liquids. The material left, which was pure white and crystalline, was dried and recrystallized at least three times from benzene. Dimethylaniline, recommended by Elbs as a solvent, was found unsuitable as it changes color when heated and the paranthracene was partially converted into anthracene at the boiling-point of this solvent. Xylene was found to be well adapted to the purpose, but benzene gave the best results. Owing to the very slight solubility of the paranthracene in benzene the following method was adopted for its recrystallization: A shell made of filter-paper and containing the material to be recrystallized was introduced into a fat-

¹ This Journal, 17, 517.

extractor, in which the extraction takes place at the boiling-point of the solvent; the lower end of the extractor was then connected with a round-bottomed flask containing *pure* benzene and the upper part with an Allihn condenser. In this apparatus when the benzene is heated to the boiling-point the extraction and filtration take place automatically so that the use of large quantities as well as any loss of the solvent is avoided. This method was found to work remarkably well with slightly soluble materials and can be highly recommended.

The products of the different crystallizations were checked by combustion analyses¹ with the following results:

First recrystallization:

0.2746 gram gave 0.9018 gram CO_2 and 0.1412 gram H_2O .

	Found.	Calculated for $\text{C}_{14}\text{H}_{10}$.
Carbon	89.56	94.38
Hydrogen	5.71	5.62
	<hr/> 95.27	<hr/> 100.00

Second recrystallization:

0.3182 gram gave 1.0885 grams CO_2 and 0.1610 gram H_2O .

	Found.
Carbon	93.29
Hydrogen	5.61
	<hr/> 98.90

Third recrystallization:

I. 0.1478 gram gave 0.5076 gram CO_2 and 0.0760 gram H_2O .

II. 0.1576 gram gave 0.5424 gram CO_2 and 0.0796 gram H_2O .

III. 0.1828 gram gave 0.6304 gram CO_2 and 0.0923 gram H_2O .

	I.	Found. II.	III.
Carbon	93.66	93.87	94.05
Hydrogen	5.71	5.64	5.64
	<hr/> 99.37	<hr/> 99.51	<hr/> 99.69

Fourth recrystallization:

I. 0.2094 gram gave 0.7229 gram CO_2 and 0.1103 gram H_2O .

II. 0.2369 gram gave 0.8201 gram CO_2 and 0.1226 gram H_2O .

III. 0.18825 gram gave 0.6517 gram CO_2 and 0.0983 gram H_2O .

¹The first and second analyses were made by W. R. O., using lead chromate and lead oxide (method of de Roode: This JOURNAL, 12, 226); the others were made with copper oxide and oxygen in an open tube, by one of the students in the laboratory, Mr. D. A. Morton, to whom we wish here to express our thanks.

	I.	Found. II.	III.
Carbon	94.15	94.31	94.40
Hydrogen	5.89	5.75	5.80
	<hr/> 100.04	<hr/> 100.06	<hr/> 100.20

From these results we may conclude that pure paranthracene and anthracene have the same percentage composition. The paranthracene is probably accompanied by some other hydrocarbon¹ containing a relatively larger proportion of hydrogen and less carbon, from which it could only be completely separated by very many crystallizations. The pure product was a beautifully white crystalline substance melting at 242°–244° C. to a light yellow liquid which on cooling solidified to a white substance, showing, however, some green discoloration, but which melted sharply at 213° (standardized thermometer). The purest specimens of anthracene and paranthracene we could prepare showed more or less of this green color after melting, so that it seemed practically impossible completely to eliminate the substance to which it is due. The solid obtained from the melted paranthracene was identified as anthracene, possessing all the characteristics of that substance, and exhibiting a well marked violet fluorescence both in the solid form and in solution. The transformation of the paranthracene into anthracene appears to be quantitative and it may be brought about at a somewhat lower temperature (230°–235°) by prolonging the heating at this point. It takes place at a still lower temperature in boiling liquids in which it is soluble, for example in boiling naphthalene (218°) and partially in dimethylaniline (192°) and even to some extent in boiling aniline (182°).

Pure paranthracene shows no trace of the violet fluorescence so characteristic of anthracene, either in the solid form or in solution, nor does it combine with picric acid to give an addition-product analogous to the red compound anthracene forms. It differs most markedly from anthracene, however, in its solubility in various liquids. While anthracene dissolves quite readily in most of the ordinary organic solvents, paranthracene is insoluble or difficultly soluble in nearly all of

¹See Thorpe's Dictionary of Applied Chemistry, Vol. 1, p. 175.

them. It is practically insoluble in methyl and ethyl alcohols, ether, carbon bisulphide, chloroform, glacial acetic acid, petroleum-benzine, acetone and acetic ether, though it is sparingly soluble in the hydrocarbons of the benzene series at their boiling-points, being more soluble the higher the boiling-point of the solvent. It is slightly soluble in boiling ethylene bromide (0.2273 gram in 100 of ethylene bromide), much more soluble in pyridine at its boiling-point (1.106 grams in 100 of pyridine), and still more soluble in boiling anisol (1.46 grams in 100 of anisol) and in phenetol (1.50 grams in 100 of phenetol).

The specific gravity of anthracene at 27° compared with water at 4° is 1.250, while that of paranthracene is 1.265 as shown by the following determinations made with the *purest* fine ground materials :

ANTHRACENE.

Gram substance.	Wt. equal vol. water.	Specific gravity at 27°.
0.3085	0.2532	1.258
0.2475	0.1674	1.253
	Average	1.256

$\frac{1.256}{1.003472} = 1.250$ specific gravity at 27° compared with water at 4°.

PARANTHRACENE.

Gram substance.	Wt. equal vol. water.	Specific gravity at 27°.
0.2612	0.2053	1.272
0.3495	0.2763	1.266
	Average	1.269

$\frac{1.269}{1.003472} = 1.265$ specific gravity at 27° compared with water at 4°.

Paranthracene differs from anthracene also in its crystal form and optical constants, as will be seen from the following report, for which we are indebted to Professor A. C. Gill of the Mineralogical Department of this University.

"Measurements of paranthracene crystals give results as follows:

1 One cubic centimeter of water at 4° will give 1.003472 cc. at 27°—Ostwald : *Physico-Chemical Measurements*.

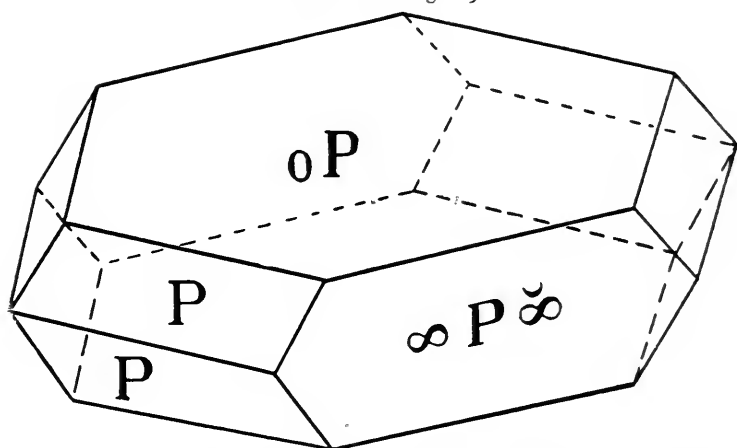
System Orthorhombic, $a:b:c = 0.6762:1:1.5731$

Faces observed, $oP(001)$, $P(111)$, and $\infty P\tilde{\infty}(010)$

Angles measured, $oP:\infty P\tilde{\infty} = 90^\circ 1'$

$oP:P = 70^\circ 24'$

$\infty P\tilde{\infty}:P = 58^\circ 9'$



“These measurements were confirmed by measurement of the plane angles on the stage of a microscope :

“Calculated angle between intersections of pyramid faces with base = $111^\circ 52'$; average of 31 measurements $111^\circ 55'$; calculated angle of pyramid intersections on the brachypinacoid $133^\circ 28'$; average of 17 measurements $133^\circ 24'$.

“The habitus of the crystals is very variable. They are usually extremely thin tabular,—much thinner than shown in the figure. Frequently the development of pyramid faces is such as to give a monoclinic appearance, more rarely an orthorhombic hemimorphic shape; and in a few cases a stout columnar form was observed. The largest crystals (from anisol) attained a length of 6 mm., with a thickness of only 0.2-0.3 mm.

“All crystals show parallel extinction on both of the pinacoids. Double refraction strong in basal plates, 0.39 as determined by interference colors. Plane of optical axes = ∞P . The positive bisectrix is normal to the base, so crystals usually give an excellent interference figure in converged polarized light. Optical angle in water with sodium light, $81^\circ 34'$.

"The close relationship of this substance to anthracene has suggested a comparison of their crystal forms. The measurements of Kokscharow¹ on anthracene are used in the comparison. The ratio $a:b$ in anthracene is 1.422:1, that of $b:a$ in paranthracene is 1.479:1. If, then, paranthracene be considered as derived from anthracene by repeated (molecular?) twinning parallel to the tabular face, the following coincidences are to be observed: (1) The paranthracene crystals are orthorhombic. (2) The corresponding lateral axes in anthracene and paranthracene are 1.422 and 1.479, respectively. (3) The tabular faces (taken as the base for each substance) coincide. (4) The pyramid faces of paranthracene should be made up of a sub-microscopic oscillatory combination, as it were, of the faces $+P$ and ∞P of anthracene. Of these, it is conceivable that ∞P should have a greater effect on the position of the pyramid faces of paranthracene, since it is more largely developed on anthracene than is $+P$. It is found, in fact, that the angle between ∞P and oP of anthracene is $68^{\circ} 30'$, that between $+P$ and oP is $82^{\circ} 22'$, while in paranthracene the angle between P and oP is $70^{\circ} 24'$, an intermediate value, but more nearly approaching the $68^{\circ} 30'$ angle.

"The relationship between the forms of these two substances would seem to afford ground for suggestive speculations on their actual stereochemical crystal and molecular structure."

The conversion of anthracene into paranthracene takes place when solutions of anthracene are exposed to the sunlight, and also less rapidly in diffused daylight. The light of the electric arc will bring about the change though much more slowly. This peculiar transformation seems to be connected in some way with the absorption of light and the fluorescence of solutions of anthracene. The radiant energy is, perhaps, partially transformed in the solutions of anthracene into chemical energy, which converts the anthracene into paranthracene, the insolubility of the latter aiding in carrying the reaction to completion.

Many attempts were made to bring about the transformation of anthracene into paranthracene by other methods, but

¹N. Petersb. Acad. Bull. 11, (1867), 385.

in no case were they successful. Some of the methods are here enumerated: paranthracene was dropped into melted anthracene at various temperatures from 215° – 240° but it was entirely converted into anthracene, the entire material solidifying as such. Anthracene suspended in concentrated hydrochloric acid was heated in a sealed tube to 220° for about seven hours. The anthracene was converted into a greenish-white pulp but was found to dissolve completely in alcohol, no trace of paranthracene being obtained. Anthracene suspended in alcohol saturated with hydrochloric acid gas was heated in a sealed tube to 220° for eight hours. No paranthracene could be detected in the material resulting. Specimens of anthracene and paranthracene heated alone in sealed tubes gave identical results. A part of the material was carbonized, but a part sublimed as anthracene in wide six-sided plates, perfectly colorless and transparent but showing an intense violet fluorescence and displaying very beautiful and striking interference-figures in converged polarized light. Some very pure anthracene was suspended in alcohol and reduced with sodium amalgam according to the method of Graebe and Liebermann,¹ and then boiled for some time with an excess of the amalgam. The conversion of the anthracene into anthracene dihydride ($C_{14}H_{12}$) was complete but no paranthracene could be detected. Anthracene dibromide ($C_{14}H_{10}Br_2$), made by the method of Perkin,² was treated with zinc dust in carbon bisulphide at about 0° , the whole mass then allowed gradually to warm up to the temperature of the room, the carbon-bisulphide solution becoming colored, first green and then brown. After evaporating off the solvent in a current of air the residue was found to consist of anthracene, zinc brouide, and a gummy material entirely soluble in alcohol, no trace of paranthracene being found. A solution of pure anthracene in benzene was treated with sodium and boiled for some time in a flask connected with a reflux condenser. No paranthracene was found in this experiment, the anthracene remaining unchanged.

Having determined that paranthracene and anthracene

¹ Ann. Chem. (Liebig) Suppl., **2**, 265.

² Chem. News, **34**, 145; Bull. Soc. chim. (Paris), [2], **27**, 465.

have the same percentage composition and that the simplest formula for both is the same, the next step was naturally the determination of the molecular weight of paranthracene, so that we might know whether anthracene and paranthracene were isomers or polymers. The molecular weight of anthracene has been determined many times by the vapor-density method as well as by the freezing- and boiling-point methods, so that its formula is known beyond a doubt to be $C_{14}H_{10}$. The vapor-density method of determining molecular weights is inapplicable in the case of paranthracene because this substance is transformed into anthracene at its melting-point (244°), while the freezing-point method gives such doubtful results, owing to the great insolubility of the material in all the solvents tried that it is also out of the question. The only method which offered any promise of success was the boiling-point method. In determining the molecular weight of paranthracene by this method we used the apparatus already described by us,¹ with ethylene bromide, pyridine, anisol, and phenetol as solvents. Owing to the slight solubility of the substance considerable difficulty was at first experienced in getting the paranthracene into such a form that it dissolved quickly in the solvent. After trying many methods we finally hit upon the plan of making the little tablets so porous and brittle that they broke into fine powder as soon as they came in contact with the boiling liquid and thus presenting a large amount of surface to the action of the solvent, dissolved immediately. To accomplish this we ground the paranthracene with alcohol to a pasty mass, which was then pressed into the shape of the ordinary tablets taking care to use as slight a pressure as possible. The tablets were then heated to 100° in an air-bath till they ceased to lose weight. In the following determinations we used paranthracene that had been crystallized at least three times and generally that which had been crystallized four times. The thermometer, which was of the Beckmann type and graduated in hundredths of a degree, was read by means of a telescope and the results were never calculated until all the readings had been taken. In every case a series was made according to the method of

¹ This Journal, 17, 517.

Beckmann. The following are the results obtained with ethylene bromide :

Paranthracene, $C_{14}H_{10} = 178$; $C_{28}H_{20} = 356$.

Solvent : Ethylene bromide,¹ ($C_2H_4Br_2$), boiling at 128.8° at 741.7 mm. Molecular rise for 100 grams $63^\circ.2$.²

Grams solvent.	Grams substance.	Observed rise.	Barometer. mm.	Mol. weight found.
195.69	0.1688	$0^\circ.030$	743.0	179
"	0.3258	$0^\circ.055$	743.0	188
190.55	0.2569	$0^\circ.035$	736.4	243
"	0.3905	$0^\circ.051$	736.4	253
176.06	0.1223	$0^\circ.014$	738.2	314
"	0.2407	$0^\circ.025$	738.1	346
184.22	0.2071	$0^\circ.020$	734.7	353
"	0.3443	$0^\circ.040$	734.7	295
181.25	0.1770	$0^\circ.018$	737.3	343
"	0.3371	$0^\circ.035$	737.3	<u>336</u>

Average of all determinations in ethylene bromide, 285

The results obtained by this method with ethylene bromide, it will be seen, are but little, if any, better than those obtained by Elbs in naphthalene by the freezing-point method. Six out of the ten values found indicate that paranthracene has a molecular weight of 356, and the average of all the determinations in ethylene bromide indicates the same fact, but the material is so slightly soluble in this solvent that the observed elevations of temperature are necessarily small. An error of observation in the hundredths place will frequently change the molecular weight from that required by a single molecule to that of a double molecule, or *vice versa*. We give these results here simply for the sake of completeness and because *at first* we were inclined to think that paranthracene was an isomer³ and not a polymer of anthracene. It was quite evident from the above determinations that a solvent must be found which would dissolve more of the paranthracene than ethylene bromide if any decisive results were to be obtained. After much time and labor we found in pyridine, anisol, and

¹ The ethylene bromide was carefully dried with calcium chloride and purified by many distillations till it had a constant boiling-point.

² This is the constant obtained by Beckmann and confirmed by us. See this Journal, 17, 526.

See *ante*.

phenetol, the solvents needed. The following are the determinations made with these liquids:

PARANTHRACENE, $C_{14}H_{10} = 178$; $C_{28}H_{20} = 356$.

Solvent: Pyridine¹ (C_5H_5N); boiling-point 114.2° at 741.7 mm. Molecular rise² for 100 grams 26.90.

Grains solvent.	Gram substance.	Observed rise.	Barometer mm.	Mol. wt. found.
97.88	0.3147	0°.024	733.3	356
"	0.6111	0°.048	733.3	350
"	0.8886	0°.077	733.3	317
88.49	0.2366	0°.020	737.2	361
"	0.3976	0°.036	737.2	338
"	0.6469	0°.056	737.2	352
92.62	0.1788	0°.014	747.7	371
"	0.4526	0°.034	747.6	387
"	0.6687	0°.054	747.6	360

Average of all determinations in pyridine, 354.

Solvent: Anisol,³ ($C_6H_5O.CH_3$); boiling-point 152.7° at 741.7 mm. Molecular rise⁴ for 100 grams 44°.3.

Grams solvent.	Grams substance.	Observed rise.	Barometer mm.	Mol. wt. found.
93.76	0.2739	0°.036	747.8	357
"	0.4956	0°.067	747.8	348
"	0.7011	0°.093	747.8	354
"	0.9012	0°.117	747.9	362
87.64	0.2610	0°.040	744.2	331
"	0.4960	0°.070	744.2	359
"	0.7212	0°.107	744.2	341
"	0.9671	0°.133	744.2	379
92.67	0.3655	0°.048	734.3	364
"	0.6350	0°.081	734.3	375
92.50	0.2279	0°.030	752.0	361
"	0.4958	0°.060	752.0	386
"	0.8236	0°.096	752.0	397

Average of all determinations in anisol, 362.

¹ The pyridine here used was a remarkably pure specimen, made from pyridine (marked C. P.) by boiling with solid caustic potash and rectifying till it was free from water and possessed a constant boiling-point.

² The molecular rise calculated from the absolute boiling-point according to the equation $K = \frac{0.0198 TM}{20.8}$ was 29.4° , but the mean of seven determinations gave 26.90 which is the value used. See This JOURNAL, 17, 526.

³ The anisol used was made by the action of methyl chloride on sodium phenolate and was carefully purified by many distillations until it had a constant boiling-point.

⁴ In this case $K = \frac{0.0198 \times 427.3 \times 108}{20.81} = 44.4^\circ$ which agrees very well with the constant determined experimentally. See This JOURNAL, 17, 527.

Solvent: Phenetol,¹ ($C_6H_5OC_2H_5$), boiling at $167^{\circ}.9$ at 741.9 mm. Molecular rise² for 100 grams $49^{\circ}.3$.

Grams solvent.	Grams substance.	Observed rise.	Barometer mm.	Mol. wt. found.
77.34	0.1619	$0^{\circ}.028$	743.8	366
"	0.3920	$0^{\circ}.070$	743.8	355
"	0.7422	$0^{\circ}.126$	743.8	373
"	1.0522	$0^{\circ}.168$	743.9	396
82.64	0.2448	$0^{\circ}.042$	745.5	346
"	0.4508	$0^{\circ}.080$	745.5	335
"	0.6034	$0^{\circ}.109$	745.5	329
"	0.8292	$0^{\circ}.144$	745.5	342

Average of all determinations in phenetol, 355.

Average of 30 determinations in pyridine, anisol and phenetol :

357.

From these results with pyridine, anisol and phenetol we must conclude that paranthracene has double the molecular weight of anthracene, and that its formula is $C_{28}H_{20}$, a result in complete accord with that obtained by Elbs. It would be preferable therefore to call paranthracene *dianthracene* and thus do away with the prefix para, which now has no meaning here and is simply misleading. Moreover, this method of naming the substance shows at once just what it is, and indeed is already in general use as is shown by such names as dipyridine, dipicoline, diquinoline, diterpene, etc., etc.

An interesting question here suggests itself regarding this change of anthracene into dianthracene, namely: is this peculiar transformation characteristic of anthracene or is it also found in the derivatives of this hydrocarbon and in other hydrocarbons. In order to answer this question solutions of anthraquinone, dihydroanthracene, dichloranthracene and anthranol were exposed to the action of sunlight for some weeks. In none of these solution was any change noticed except in the case of anthranol which first turned green, then yellow, a white crystalline material separating out, very different in appearance from anthranol. On evaporating off the solvent (benzene) a nearly white product was obtained which turned brown and melted not very sharply at 265° – 270° C., evidently

¹ The phenetol used was a very pure specimen which was carefully purified and subjected to quite a number of distillations before being used.

² This constant was experimentally determined. See This JOURNAL, 17, 528.

undergoing some sort of decomposition. This substance was less soluble in the ordinary solvents than anthranol and was completely insoluble in solutions of the alkalies even on long boiling. From its high melting-point (anthranol melts at 163° – 170° , according to Liebermann), slight solubility and method of formation this substance would seem to be dianthranol, a dihydroxyl derivative of dianthracene, though further work must be done to show whether this view be correct or not. Unfortunately none of the higher homologues of anthracene were obtainable so that it is not possible to state whether they would polymerize in the same way as anthracene or not. Solutions of *pure* phenanthrene, retene, camphor and phenylacridine were also found to suffer no change in the sunlight, so that the transformation would seem to be due to some peculiarity of the anthracene molecule. Of all the substances which bear any relation to anthracene perhaps acridine, $C_{13}H_9N$, resembles anthracene most closely. This was shown very strikingly when solutions of acridine were exposed to the direct action of the sunlight. A light yellow crystalline coating formed on the sides of the bottles as in the case of anthracene solutions. This substance was exceedingly insoluble in all solvents tried, did not unite with acids to form salts as acridine does so readily, and on heating slowly to 250° volatilized without melting, the volatilized portion melting at the melting-point of acridine, dissolving in acids with the characteristic greenish fluorescence and exhibiting all the other properties of acridine. Heated rapidly the insoluble product melts at 276° , the melted mass after solidification melting at 107° (the melting-point of acridine), and showing all the other characteristic properties of acridine. This insoluble acridine is also converted into acridine by boiling for a long time in liquids in which it is slightly soluble. No further work was done with this substance, as its insolubility rendered purification impossible and even if it could be purified there is no way of determining its molecular weight. Whether this substance be diacridine and whether it be identical with the product obtained by Graebe and Caro¹ by the action of sodium amalgam on an alcoholic solution of acridine

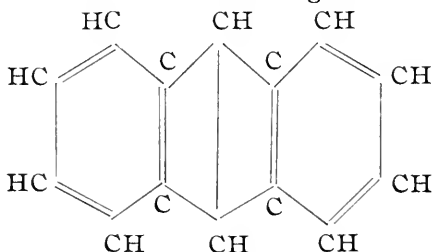
¹Ann. Chem. (Liebig), **158**, 278.

and called by them insoluble hydroacridine,¹ remains an open question.

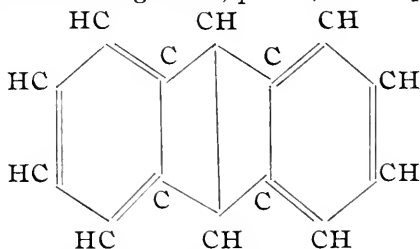
It is perhaps worth while to note here that Bernthsen and Bender found² that phenylacridine when reduced with sodium amalgam in alcohol did not give an insoluble compound analogous to the so-called insoluble hydroacridine of Graebe and Caro. This agrees with the observation made by us that phenylacridine solutions undergo no change in the sunlight analogous to that noted in the case of acridine itself.

THEORETICAL.

In order to express the relation existing between anthracene and dianthracene by structural formulas it will be necessary first to discuss the various formulas that have been proposed for anthracene and determine which one of these best represents the facts. The formula in general use



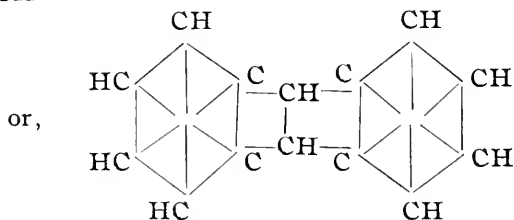
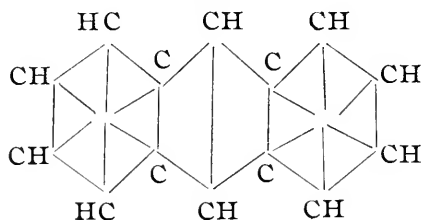
is one that was first proposed by Graebe and Liebermann in their celebrated paper on anthracene and alizarin. This formula is the one found in most text-books and is the one most generally accepted, though a second formula proposed by Behr and Van Dorp, and given by Seelig in his book *Organische Reactionen und Reagentien*, p. 620, is also possible:



¹ For another suggestion regarding the structure of this substance, see Ber. d. Chem. Ges. **16**, 1973.

² *Ibid.* **16**, 1972.

The so-called quinoid formula of Armstrong, the prism formula of Wegscheider, and the centric formula of Bamberger for anthracene are not here considered as they do not represent the chemical conduct of anthracene as well as the other formulas which have been proposed. Besides these two formulas there is a third, which has not yet been proposed, so far as we are aware, for anthracene, but which we think is preferable to the other two:



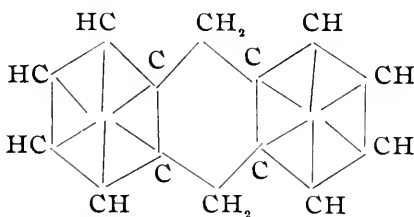
It is merely the application of the idea of centric bonds to the anthracene molecule, but should not be confused with the formula suggested by Bamberger.¹

von Baeyer has shown that in benzene and the carboxylic acids derived from it the centric formula best represents the relation of the atoms. One of the principal reasons for this view is the extraordinary stability of benzene particularly towards oxidizing agents, such a powerful reagent as an alkaline solution of potassium permanganate having no action on this hydrocarbon. Now anthracene yields on oxidation anthraquinone, a substance which is especially characterized by its stability towards the most powerful oxidizing agents. In this oxidation of anthracene to anthraquinone neither of the benzene rings is affected, the so-called meso ring being the one that undergoes the change. Anthraquinone may be made from benzoic acid or phthalic acid and yields benzoic

¹ Ann. Chem. (Liebig), **257**, 52.

acid when fused with solid caustic potash at a comparatively high temperature. Anthracene itself may be made synthetically from benzene and symmetrical tetrabrommethane, and that it contains two benzene residues must be accepted from this and other considerations. It seems highly probable, therefore, that if the centric formula be regarded as the correct representation of the condition of the atoms in benzene, benzoic, and phthalic acids, it must also be accepted for the benzene residues in anthraquinone and consequently in anthracene itself.

When anthracene is reduced in alcoholic solution by means of sodium amalgam it yields very readily dihydroanthracene, a substance which can be further reduced only by the action of the most powerful reducing agents, such as hydriodic acid and phosphorus. In this respect it will be seen that dihydroanthracene closely resembles benzene itself, as we should naturally expect if it were made up of two benzene residues united by two CH_2 -groups as represented in the formula

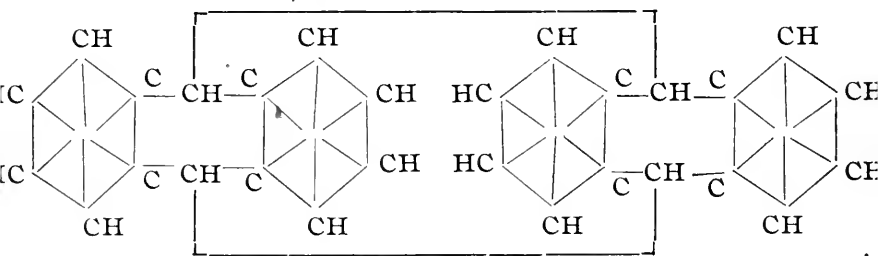


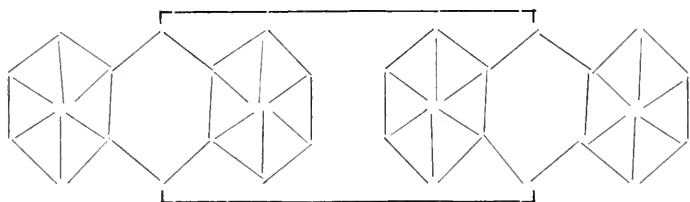
This centric formula for anthracene is, further, in accord with the fact that it is the γ -carbon or hydrogen atoms that are almost invariably the ones first affected when this hydrocarbon is acted on by the various reagents, the only exception being in the case of the action of sulphuric acid, which substitutes two of the benzene hydrogen atoms by sulphonic acid groups—conduct in entire accord with the idea that the meso ring is made up of a paraffin residue which should not be affected by sulphuric acid.

It will be seen on examining the formula proposed for anthracene that it represents that molecule as made up of two benzene rings, and two meso rings of four carbon atoms having two of these carbon atoms in common, and not as composed of three

benzene rings as usually stated. This will explain the difference in chemical conduct between this hydrocarbon and its isomer, phenanthrene, which actually does contain three rings of six carbon atoms.

When anthracene is either oxidized or reduced it yields readily compounds containing two benzene rings and one middle ring of six carbon atoms. As the tendency of carbon compounds to form rings containing six carbon atoms is very great this may explain why anthracene is so easily oxidized and reduced. Not only is this true but the fact that anthracene so readily polymerizes forming dianthracene, is also easily understood. For that dianthracene does not contain a para bond connecting the γ -carbon atoms must be assumed from the fact that it does not exhibit the fluorescence so characteristic of anthracene and its derivatives containing the para bond¹, and that it does not yield addition-products with chlorine or bromine nor with picric acid, as anthracene so readily does. It is quite probable, therefore, that the change of anthracene to anthraquinone, to dihydroanthracene, and to dianthracene are all due to the same cause: the presence in the anthracene molecule of the two middle rings of four carbon atoms and the general tendency so often noted in carbon compounds to form six-membered rings. The stability of anthraquinone towards oxidizing agents, of dihydroanthracene towards reducing agents, and of dianthracene towards reagents in general, thus receives a simple explanation. These considerations lead to the formula

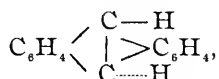




for dianthracene, very similar to the one suggested by Linebarger, though it will be observed that his statement that it contains a ring of four carbon atoms is erroneous. This formula is best represented by using solid models. Then, of course, the second half of the formula would be represented as superimposed on the first.

This formula for dianthracene will explain the transformation of this substance into anthracene under the influence of heat, the conversion of anthracene into dianthracene in the direct sunlight, the stability of dianthracene, and the fact that when it is acted on by reagents it gives derivatives of anthracene, being apparently first transformed into that hydrocarbon.

The crystallographic study of anthracene and dianthracene is also in accord with the formulas proposed for these substances. Assuming for anthracene the *trans* formula¹



it will be noted by consulting the stereochemical model that it represents a monoclinic symmetry and anthracene crystallizes in the monoclinic system, as Kokscharow has shown and as Dr. Gill has proved by a remeasurement of the crystals and a careful study of their optical properties. The stereochemical model of the dianthracene formula, on the other hand, represents an orthorhombic symmetry while dianthracene crystallizes in the orthorhombic system, according to the very careful measurements of Dr. Gill. The coincidences noted and enumerated by him between the anthracene and dianthracene crystals on the supposition that dianthracene is derived from anthracene by molecular twinning are also very

¹ The dotted line represents the hydrogen atom below the plane of the paper, the unbroken line the one above.

striking, and receive a ready explanation on the assumption of the above formulas. The specific gravity of anthracene and dianthracene are also in accord with these theoretical considerations.

The only other substances which were found to undergo a similar transformation to that observed in the case of anthracene were anthranol and acridine. To be sure it was not possible to determine whether the insoluble acridine was diacridine and that the change was strictly analogous to that of anthracene into dianthracene; still it is significant that both anthracene and acridine contain a "para" bond and both yield insoluble modifications when their solutions are exposed to the action of the direct sunlight. Whether the substances obtained from pyridine and quinoline by the action of sodium and called dipyridine and diquinoline, are similar in structure to dianthracene and whether their formation is due to the para bond in pyridine and quinoline remains yet to be proved; but there would seem to be no reason against such a supposition. It is to be noted in this connection that substances which do not contain a para bond, like anthraquinone and dihydroanthracene, suffered no change in the sunlight. Phenanthrene, too, isomeric with anthracene, undergoes no change when its solutions are exposed to the action of the sunlight.

The polymerizing action of light appears to have been but little studied and to have been observed only in connection with the polymerization of unsaturated compounds, if we except the observation that maleic acid is transformed into its isomer, fumaric acid, in the presence of a trace of bromine and in the sunlight.

A solution of sulphur or phosphorus in carbon bisulphide undergoes a change in the direct sunlight very similar to that observed in the case of solutions of anthracene. An insoluble modification is precipitated from the solution and the emergent light is destitute of the ultra-violet rays, while the less refrangible luminous part of the spectrum is unaltered. Apparently here the chemical rays are absorbed and expended in the production of chemical work. Whether the insoluble sulphur and the red phosphorus are polymeric modifications

of the ordinary sulphur and phosphorus can only be conjectured at present.

In the case of anthracene the change would seem to be closely connected with the strong absorption-bonds observed by Hartley in its solutions and with the fluorescence of this substance. Solutions of acridine and anthranol also show a bluish fluorescence in reflected light, and it would be interesting to compare the absorption-spectra of anthracene, dianthracene, anthranol, dianthranol, acridine and the insoluble acridine with reference to this subject.

Further work with a view to preparing derivatives of dianthracene will be undertaken in this laboratory.

Contributions from the Laboratory of Analytical Chemistry of the University of Michigan.

ON THE OXIDATION OF SOME GASES WITH PALLADINIZED COPPER OXIDE.

BY E. D. CAMPBELL.

In the work heretofore done on the combustion of gases where the well-known influence of finely divided palladium upon the ignition of gases has been taken advantage of, the oxygen for the combustion of the gas under examination has been introduced either as pure oxygen or diluted with nitrogen in the form of air. It was thought not impossible if palladium in sufficiently fine form and evenly distributed could be introduced into a solid reagent capable of giving up oxygen to combustible gases, that the temperature at which gases containing hydrogen would burn, might be lowered below the combustion-point in the absence of palladium, and that the differences in the temperatures of combustion of various gases might lead to a system of fractional combustion.

Copper oxide, being one of the most common reagents for combustion and having the great advantage over most others of being easily reoxidized after reduction, was thought to be the most desirable substance to work upon. Copper oxide containing palladium very finely divided and evenly distributed throughout, was prepared in three ways; of these the first by which the oxide used in the combustion shown in the table was made, was as follows :

An alloy was prepared by melting 600 grams of fine copper and then adding 6 grams of palladium. After melting, this alloy was cast into a cold iron mould, then broken up and re-melted at a temperature nearly approaching the melting-point of palladium (considerably above that of copper), then quickly recast into cold iron moulds, the strips so cast being about 12 mm. wide and 5 mm. thick. Palladium did not seem to alloy very readily with copper, so that it was necessary to re-melt at a high heat and cool quickly to prevent the palladium from distributing itself in the form of a fine network, which rendered the alloy brittle when attempts were made to roll it. By re-melting at a high heat and quickly cooling an alloy was produced in which the palladium was evenly distributed and which rolled as easily as pure copper. The strips of alloy thus produced were annealed like pure copper, then rolled until the thickness was reduced to 0.3 mm., the width remaining about the same. These strips were then cut transversely into pieces 1.5 mm. wide, thus giving small pieces 12 mm. long, 1.5 mm. wide, and 0.3 mm. thick. About 160 grams of this alloy was introduced into a combustion-tube of 16 mm. internal diameter, the alloy being retained in position at both ends by plugs of copper gauze. The column of alloy was 34 cm. long. The combustion-tube so prepared was placed in an ordinary Bunsen combustion-furnace, brought to a moderate red heat, and purified oxygen passed through as long as it was taken up.

Second Method.—In the course of the work, owing to frequent reduction and re-oxidation of the copper and to handling of the oxide in filling or emptying tubes, a considerable amount of fine oxide accumulated which could not be used as it was without choking the tube. This fine oxide was ground until it would pass through a 100-mesh sieve, mixed with thick mucilage to a rather stiff paste and pressed by means of a sodium press into wire a little less than 2 mm. in diameter. This wire, after it had become dry, was broken into pieces about 10–12 mm. long, introduced into a platinum crucible and heated to a moderate red heat until all volatile matter ceased coming off. The wire so produced was strong enough to retain its form perfectly while introducing it into a

combustion-tube in which it could be completely oxidized by means of oxygen at a red heat.

Third Method.—This method was not worked out until the combustions shown in the table were completed, but it is recommended as the best method for the purpose of preparing the oxide, as it is much simpler than either of the previous methods, and the oxide prepared by it we have shown by quantitative combustion of hydrogen is fully as efficient as that produced by the first or second method. The method is as follows: 3 grams of palladium wire was dissolved in a moderate-sized casserole by means of 40 cc. of nitric acid (sp. gr. 1.42) to which was added 10 cc. of hydrochloric acid (sp. gr. 1.20). After evaporating to dryness on the water-bath the palladium was brought into solution with 10 cc. of nitric acid, 3 cc. of hydrochloric acid and sufficient water to bring the volume to 60 cc. Into this solution was introduced 300 grams of pure copper oxide, previously ground to pass through a 100-mesh sieve. This produced a very stiff paste, which after thorough mixing was dried at 120° and again ground to pass through a 100-mesh sieve. The fine ground oxide so produced was then mixed with mucilage, pressed into wire, dried and ignited like that in the second method of preparation.

In order to control the temperature of the tube at any time a special form of air jacket was made, in two halves, so that it could be put on when the combustion-tube was used for combustion, or removed when it was desired to re-oxidize the copper without disturbing the position of the tube. The jacket consisted of two halves of a heavy brass tube 3 mm. thick, 52 mm. internal diameter, and 48 cm. long; this internal diameter allowed the jacket to surround the combustion-tube and its gutter and still leave a clear space of 5 to 7 mm., thus heating the tube entirely by radiation. The thickness of the inner brass tube also tended to equalize the temperature and to prevent sudden variations. The two halves of this inner brass tube were joined at both ends to an outer heavy sheet-iron tube, leaving between the tubes an annular space of 7 mm. The two halves of outer sheet-iron tube came together on the under side in the form of a lap joint and were

prolonged on the upper side so as to be supported by means of metal pins on both sides of the double horizontal bar at the top of the furnace usually used to keep the tiles apart. Through the double bar at the top of the furnace and through three holes in the inner brass tube, were introduced three nitrogen-filled thermometers capable of registering 460° . These thermometers reached to and rested on the inner combustion-tube. In addition to this jacket on each side of the furnace were provided two sheet-iron guards to prevent currents of air and to maintain a steadier heat. In addition to these a heavy sheet-iron gutter 54 mm. wide and 48 cm long, was curved to fit the under side of the outer jacket and when wired to it could take the direct heat of the flame and prevent the burning out of the outer jacket. This gutter was found necessary when working at the higher heats. Thus provided, the inner combustion-tube was so placed that it was heated by radiation from the heavy inner brass tube which was in turn heated by radiation from the outer sheet-iron jacket. In this way a steady, even temperature of the combustion-tube could be maintained at any temperature up to 450° , and the entire jacket could be easily removed, the tiles put back in their usual place and the copper reoxidized without disturbing the combustion-tube.

In determining the initial combustion-point of any gas a moderate flow of the pure gas was kept passing through the combustion-tube, to the farther end of which was attached a small tube containing glass-wool sprinkled with anhydrous cupric sulphate, for the detection of moisture, followed by a U tube containing a clear solution of calcium hydrate for the detection of carbon dioxide. The temperature of the tube was gradually raised, the three thermometers being kept within a range of 5° until a test for moisture and carbon dioxide was obtained. As soon as this was done in any case the supply of gas was shut off and pure dry air drawn through the tube, the temperature allowed to fall below the ignition-point, the gas turned on again and the temperature again carefully brought up until a second test was obtained. In gases containing both carbon and hydrogen, a test for carbon dioxide was obtained always a little in advance of that for

moisture. This difference is probably accounted for by the greater sensitiveness of calcium hydrate for carbon dioxide than that of anhydrous cupric sulphate for moisture. In the table of results, the limits of temperature given include those at which distinct test for both moisture and carbon dioxide were obtained. In determining the ignition-point of a gas it was also found necessary to use the combustion-tube after it had been used for a quantitative combustion, since a freshly reoxidized tube was found to contain small amounts of palladium oxide, which gives up its oxygen very much more readily than the copper oxide and which would consequently make the ignition-point apparently much lower than its true value.

For the quantitative combustion of gases, the inlet end of the combustion-tube was connected to a T tube provided with a three-way stop-cock by means of which either the pure dry gas under examination could be introduced into the tube, or by reversing the cock pure dry air or oxygen could be drawn or forced through the tube for the purpose of sweeping forward the products of combustion or for reoxidizing the copper when desired.

In determining the rate of combustion of any gas the method was as follows: The tube filled with air was carefully brought up to the temperature at which combustion was to be made and maintained at this temperature until thoroughly heated through. A weighed calcium-chloride tube was attached to the outlet of the combustion-tube, followed by a double Liebig potash-bulb. The latter was made by uniting two ordinary Liebig bulbs and placing in the first bulb a solution of potassium hydroxide (1 : 2), and in the second bulb a stronger (1 : 1), the bulb being provided with the usual guard-tube. It was found necessary to have the potassium hydroxide in the first bulb more dilute than 1 : 1, since most of the carbon dioxide was taken up in the first small bulb, and if 1 : 1 potassium hydroxide was used potassium acid carbonate crystallizes out so as to choke the tube. By using the more dilute solution in the first bulb the trouble is avoided. When the combustion-tube has attained the desired temperature, the pure gas under examination was forced through

the tube, the rate at which it is supplied being so regulated that as light excess of unburned gas passes completely through the train. In the combustions shown in the table this excess of unburned gas was judged by the number of bubbles passing through the last small bulb of the potash bulbs, and the supply of gas was so regulated that this excess should come through at the rate of 6-10 bubbles per minute. The exact time at which the gas was introduced into the combustion-tube was noted. The gas at the commencement was introduced rather rapidly for a few moments to expel the air in the tube, then the flow regulated to the 6-10 in excess and kept up for times varying from 45 minutes to 6 hours, according to the rate at which the gas burned. At the end of an exact time, the stopcock was reversed and pure air drawn through the tube until all the products of combustion had been collected. From the weight of water and of carbon dioxide or of both obtained, the number of cc. of pure gas required to produce these was calculated. In addition to the number of cc. of each gas burned per hour has been calculated the weight of oxygen removed from the copper oxide for the combustion. In order to determine the extent to which palladium effected combustion, the ignition-point of the various gases was determined by passing the gas over a long plug of pure copper oxide made by oxidizing pure copper gauze. This copper oxide was contained in a combustion-tube of the same size and heated in the same way as the one containing the palladinized copper oxide. It will be noted that the ignition-point of hydrogen has been reduced about 95° , that of ethylene 75° , of propylene 50° , of isobutylene 40° , while that of carbon monoxide, as would be expected, has not been affected.

In the preparation of gases the following methods were used :

I. Hydrogen was prepared by the action of dilute sulphuric acid on pure zinc and purified by passing through potassium hydroxide (1:1), over dry potassium hydroxide, calcium chloride and phosphorus pentoxide.

II. Carbon monoxide was prepared by the action of strong sulphuric acid upon oxalic acid, the carbon dioxide being re-

moved with potassium hydroxide and the gas being then purified in the same way as the hydrogen.

III. Ethylene was prepared by the action of ethyl alcohol upon phosphorus pentoxide and purified by passing through strong potassium hydroxide and then over three towers of dry potassium hydroxide. It was found in the course of the work that if phosphorus pentoxide was used in the train that there was some polymerization with ethylene and that this tendency to polymerize increases with propylene and was so marked with isobutylene as entirely to prevent the use of phosphorus pentoxide. Ethylene produced from alcohol and sulphuric acid in the usual manner was found to contain so much carbon monoxide as to be unfit for this work, while that produced by the method used was shown by analysis to be practically pure.

IV. Propylene was prepared by carefully heating propyl alcohol and phosphorus pentoxide and purifying as in the case of ethylene. This method gives very nearly if not quite pure propylene.

V. Isobutylene was prepared by the action of isobutyl iodide upon alcoholic potash, the gas being collected over a 10 per cent. solution of common salt and then purified in the same way as ethylene and propylene. When an attempt was made to obtain isobutylene by the action of the corresponding alcohol upon phosphorus pentoxide, it was found the resulting gas contained only about 60 per cent. of isobutylene and 35 per cent. of butane.

VI. Methane was prepared by the action of methyl iodide on zinc-copper couple immersed in alcohol. It was purified by passing through strong sulphuric acid containing chromic acid and then through strong potassium hydroxide, followed by dry potassium hydroxide and phosphorus pentoxide.

VII. Acetylene was prepared by the action of calcium carbide on water. It was purified and dried by passing through strong potassium hydroxide and then over dry potassium hydroxide.

The details of the temperature and rate of combustion of the above gases, except acetylene, which does not oxidize perfectly to carbon dioxide and water, are shown in the fol-

lowing table. All rates of combustion have been calculated from the weight of water or carbon dioxide obtained to the cc. of pure dry gas, under standard conditions, which would be burned in one hour. Since these combustions were all made in the same sized tube and with practically the same amount of surface of copper oxide exposed the rates of combustion are comparable. Of course varying the size of the combustion-tube and with it the amount of palladinized copper oxide present would alter the absolute rates of combustion but would probably not effect the relative rates.

In the case of easily burned gases, like hydrogen and carbon monoxide, it is not found necessary to re-oxidize the tube after each combustion, but in the case of more difficultly burned gases this was found desirable, especially when burning at the higher temperatures and when the previous combustion had removed a good deal of oxygen.

Exp. No.	Gas.	Initial combustion point with palladinized copper oxide.	Initial combustion point with pure copper oxide.	Temp. of combustion.	Length of time in hours.	Wt. H ₂ O.	Wt. CO ₂ .	cc. of gas burned per hour.	Wt. O ₂ removed per hour.
1	H ₂	80-85°
2	H ₂	175-180°
3	H ₂	115-120°	6	0.4808	99	0.0713
4	H ₂	125-130°	6	1.295	266.4	0.1918
5	H ₂	135-140°	6	1.974	406.2	0.2925
6	H ₂	145-150°	6	3.544	729.2	0.525
7	H ₂	165-170°	6	3.688	754.8	0.5435
8	CO	100-105°
9	CO	100-105°
10	CO	125-130°	6	0.669	56.4	0.0406
11	CO	135-140°	6	1.0215	86.1	0.062
12	CO	145-150°	6	2.313	196.7	0.1403
13	CO	155-160°	2½	2.101	425.1	0.3059
14	CO	175-180°	1½	1.7685	599.5	0.4292
15	CO	195-200°	1½	1.951	654.9	0.4734
16	C ₂ H ₄	240-250°
17	C ₂ H ₄	315-325°
18	C ₂ H ₄	270-275°	2	0.0515	0.116	14.7	0.063
19	C ₂ H ₄	295-300°	2	0.111	0.268	33.8	0.145
20	C ₂ H ₄	325-330°	2	0.3215	0.815	103.	0.442
21	C ₂ H ₄	345-350°	2	0.489	1.1725	148.5	0.636

Exp. No.	Gas.	Initial combustion point with palladium copper oxide.	Initial combustion point with pure copper oxide.	Temp. of combustion.	Length of time in hours.	Wt. H ₂ O.	Wt. CO ₂ .	cc. of gas burned per hour.	Wt. O ₂ removed per hour.
22	C ₂ H ₄	370-375°	2	0.565	1.3665	172.8	0.741
23	C ₂ H ₄	395-400°	2	0.5985	1.4555	184.	0.789
24	C ₂ H ₄	420-425°	2	0.742	1.830	231.4	0.993
25	C ₂ H ₄	450-455°	1½	0.561	1.388	234.	1.004
26	C ₃ H ₆	220-230°
27	C ₃ H ₆	270-280°
28	C ₃ H ₆	240-245°	2	0.0315	0.0475	4.	0.0257
29	C ₃ H ₆	270-275°	2	0.0905	0.179	15.1	0.0972
30	C ₃ H ₆	295-300°	2	0.2345	0.569	48.	0.3089
31	C ₃ H ₆	320-325°	2	0.9505	2.332	196.5	1.265
32	C ₃ H ₆	345-350°	2	1.265	3.092	260.5	1.6695
33	C ₃ H ₆	370-375°	2	1.2505	3.0125	253.8	1.634
34	C ₃ H ₆	395-400°	2	1.271	3.0765	259.3	1.668
Iso.									
35	C ₄ H ₈	270-280°
36	C ₄ H ₈	320-330°
37	C ₄ H ₈	270-275°	2	0.051	0.196	7.87	0.0755
38	C ₄ H ₈	295-300°	2	0.185	0.559	28.57	0.2454
39	C ₄ H ₈	320-325°	2	0.6765	1.8665	104.4	0.895
40	C ₄ H ₈	340-345°	2	1.6495	4.036	254.8	2.186
41	C ₄ H ₈	370-375°	¾	1.431	3.4775	588.6	5.059
42	CH ₄	No combustion at 455°.							

In the above table all of the quantitative combustions were performed with palladinized copper oxide, prepared by the first method, the ignition-point only of the various gases being determined with pure copper oxide in order to determine to what extent the presence of 1 per cent. of palladium affected the temperature at which combustion commenced. In the calculation of the rate of combustion of ethylene and of propylene (experiments 18-25 and 28-34), the volume was calculated from the amount of carbon dioxide since, owing to the use of phosphorus pentoxide in one arm of the U tube used for collecting the water, there was slight polymerization, which made the amount of water a little higher than the true value. On the other hand, in the case of isobutylene (experiments 37-41) the rate of combustion was calculated from the amount of water produced, the U-tube being filled with calcium chloride

alone, thus avoiding polymerization. The solubility of isobutylene rendered the carbon dioxide a little in excess of the amount calculated for perfect combustion so that it was thought to be more accurate in this case to use the weight of water rather than that of carbon dioxide in calculating the rate of combustion.

In all of the gases on which quantitative combustions were made, although a slight excess of unburned gas was forced completely through the train, if the supply was slackened a little, perfect combustion took place and no unburned gas escaped. In the case of methane no combustion took place at 455° , and, as 460° was the limit to which nitrogen-filled thermometers could be carried, it was found necessary to lay aside the work so far as the paraffins go until suitable modifications to the furnace can be made by means of which such temperatures as may be necessary for the combustion of these gases can be obtained and controlled, when the work will be continued. After obtaining the temperature of ignition and rate of combustion of the ordinary gases occurring in the pure state, mixtures of these gases will be worked upon in order to determine if possible to what extent they may be separated by fractional combustion. The combustion of acetylene differs from that of any of the gases given in the above table, since this gas does not burn at once to carbon dioxide and water, but undergoes a series of rather complex decompositions which would render it incapable of being separated by fractional combustion. In attempting to determine the ignition-point of acetylene, the pure dry gas was passed through a tube containing palladinized copper oxide, having a small tube of anhydrous cupric sulphate attached to the farther end, followed by a U-tube containing calcium hydroxide for the detection of carbon dioxide. A steady flow of gas was kept up through the tube, which was very slowly heated; no apparent change occurred until a temperature of 225° – 230° was reached, when the first test for moisture was observed, but no carbon dioxide. The flow of gas was kept up, the temperature of the tube being gradually raised until a temperature of nearly 300° was reached, when the tube was found to be choked up although no test for carbon dioxide had as yet been obtained. On re-

moving the combustion-tube from the furnace the palladinized copper oxide nearest the inlet of the tube was found to be filled for a distance of about 5 cm. with a heavy black deposit. The combustion-tube was refilled with fresh palladinized copper oxide prepared by the second method, heated to nearly 300° and acetylene once more turned through the tube and the temperature raised, when a test for carbon dioxide was obtained at $315-320^{\circ}$. On removing the jacket from the furnace a deposit similar to the first was observed, but not in sufficient quantity to choke the tube; this deposit was removed by heating the tube to a red heat and forcing in oxygen until everything was burned. After thus re-oxidizing the tube the jacket was replaced and the temperature raised to and maintained at 345° . Acetylene was turned into the tube at such a rate that 3-5 bubbles per minute passed through the last bulb of the weighed potash bulb used for regular quantitative combustion. This was kept up for two hours, when it was found that the water obtained weighed 0.3171 gram and the carbon dioxide 0.4834 gram. If combustion had been perfect to carbon dioxide and water, then the amount of water obtained should have been accompanied by 1.547 grams carbon dioxide instead of less than one-third this amount. On removing the jacket a deposit similar to the previous ones was observed which was removed by oxidation at a red heat. A second quantitative combustion was then made, the temperature being $395-400^{\circ}$. In this combustion the amount of water obtained was 0.4056 gram accompanied by 1.4753 grams carbon dioxide—a little greater ratio than the previous one. After removing the jacket the carbonaceous deposit was again removed by burning at a red heat and the water and carbon dioxide produced were weighed. This gave: water, 0.0521 gram and carbon dioxide, 0.7737 gram. From these results we see that when acetylene is passed through a tube of palladinized copper oxide at a temperature of $395-400^{\circ}$ two-thirds of the carbon and eight-ninths of the hydrogen are oxidized to carbon dioxide and water respectively, while one-third of the carbon and one-ninth of the hydrogen remain in the tube in a form as yet undetermined.

In a combustion similarly conducted but with the tempera-

ture at 445° – 450° the amount of water obtained in the same length of time was 0.6747 gram accompanied by 1.9486 grams of carbon dioxide, thus showing that while the rate at which dissociation took place increased with rise in temperature, oxidation did not seem to reach a higher limit than at 400° .

Credit is due Messrs. R. F. Flinterman, C. R. Rose and E. B. Hart for the care with which they have carried out the laboratory work of the above research.

ANN ARBOR, July, 1895.

NOTES ON LIMONENE AND ITS DERIVATIVES.

BY EDWARD KREMERS.

Rotatory Power of Limonene.

In the contribution on "Terpene und Aetherische Oele,"¹ containing a report of the specific rotatory power of a number of terpenes and derivatives, by Wallach and Conradi, the following values for $[\alpha]_D$ for the limonenes are given :

Dextrogyrate Limonene, $+106.8^{\circ}$;

Leavogyrate Limonene, -105° .

About five years ago, while working on the interesting phases of isomerism manifested by the limonene group of "terpenes," now terpadines, I made the observation that the $[\alpha]_D$ of a freshly distilled limonene was 121.3° .² This determination was made upon the pure oil without a solvent. A few months later a chloroform-solution containing 18.74 per cent. of oil was observed to have a specific rotatory power of 106.01° . Still later the $[\alpha]_D$ of a chloroform-solution containing 22.34 per cent. of the same oil was 101.01° . Without the use of a solvent $[\alpha]_D$ was determined to be 103.23° .

The diminution of the rotatory power was accompanied by an increase in the specific gravity of the hydrocarbon. Although my data were very meagre at the time, I ventured to express this opinion: "It is apparent that chloroform has but slight influence on the rotatory power of limonene. The

¹ Ann. Chem. (Liebig), **252**, 145.

² Isomerie verhältnisse innerhalb der Terpenreihe—Inaugural Dissertation: Goettingen, 1890, p. 18.

increase of the specific gravity and the decrease of the rotatory power show that limonene changes slowly but perceptably upon standing."

Last summer Mr. Edward A. Mayer had occasion to fractionate carefully several pounds of commercial "carvene." As a result a considerable quantity of pure limonene, *i. e.*, as pure as it could be obtained from this source by fractional distillation, was obtained. With such material at our disposal it seemed desirable to ascertain what influence some of the more common solvents exert upon the rotatory power of this hydrocarbon. For this purpose the fraction boiling between 174.5° – 175° was employed. Its specific gravity at 20° was 0.8456; its $[\alpha]_D$ was $+120.466$, *i. e.*, without solvent.

The data compiled in the following tables make it readily apparent that the solvents employed—absolute and ordinary alcohol, chloroform and glacial acetic acid—diminish the rotatory power of limonene. In the case of absolute alcohol and chloroform the rotatory power of the limonene seems to diminish with fair regularity as the quantity of solvent increases. In the case of the glacial acetic acid no such regularity is apparent. The data obtained with ordinary alcohol are not sufficient to warrant any general statement, though here also the few data obtainable point toward the same conclusion.

A short table of physical constants, *viz.*, specific gravity and $[\alpha]_D$ for the fractions just below and just above the limonene fraction, has also been appended, because it shows what influence the other constituents of caraway oil have on the specific gravity and rotatory power of the limonene.

These tables were compiled by Mr. Edward A. Mayer from the data obtained by him shortly after the fractionation of the oil.

SOLUTION IN ORDINARY ALCOHOL.

Fraction.	Percentage of oil.	Sp. gr. at 20° .	α^1 .	$[\alpha]_D^1$
174.5 – 175°	10	0.8180	$9^{\circ}.159$	$111^{\circ}.968$
	20	0.8201	$18^{\circ}.517$	$112^{\circ}.894$
	30	0.8247	$28^{\circ}.131$	$113^{\circ}.701$

¹ Throughout these tables the sign is +.

SOLUTION IN ABSOLUTE ALCOHOL.

Fraction.	Percentage of oil.	Sp. gr. at 20°.	α .	$[\alpha]_D$.
174.5-175°	10	0.7975	9°.046	113°.430
	20	0.8005	18°.241	113°.940
	30	0.8071	27°.716	114°.470
	40	0.8133	37°.600	115°.570
	50	0.8172	47°.500	115°.690
	60	0.8235	57°.500	116°.373
	70	0.8286	67°.700	116°.720
	80	0.8349	73°.660	117°.768
	90	0.8409	89°.331	118°.036
	100	0.8456	101°.866	120°.466

SOLUTION IN CHLOROFORM.

10	1.3801	15°.964	115°.673
20	1.2873	29°.771	115°.633
30	1.2081	42°.362	116°.844
40	1.1445	53°.716	117°.335
50	1.0827	63°.665	117°.604
60	1.0273	72°.875	118°.230
70	0.9769	81°.152	118°.672
80	0.9335	89°.185	118°.209
90	0.8928	95°.405	118°.733
100	0.8456	101°.866	120°.466

SOLUTION IN GLACIAL ACETIC ACID.

10	1.0229	11°.814	115°.495
20	0.9980	22°.696	113°.707
30	0.9738	33°.202	113°.650
40	0.9537	43°.395	113°.753
49.881	0.9337	53°.547	114°.971
60	0.9124	63°.695	116°.350
70	0.8946	72°.668	116°.041
80	0.8789	81°.796	116°.332
90	0.8641	90°.866	116°.841
100	0.8456	101°.866	120°.466
172.5-173°	0.8455	99°.483	117°.662
173 -173°.5	0.8453	100°.733	119°.168
173.5-174°	0.8446	101°.189	119°.807
174 -174°.5	0.8443	101°.883	120°.672
174.5-175°	0.8456	101°.866	120°.466
175 -175°.5	0.8486	99°.273	116°.984
175.5-176°	0.8507	97°.887	116°.242
176 -177°	0.8536	97°.275	113°.958

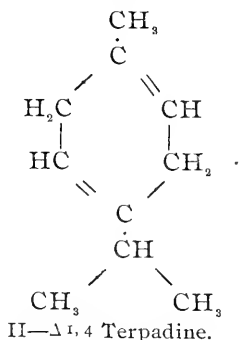
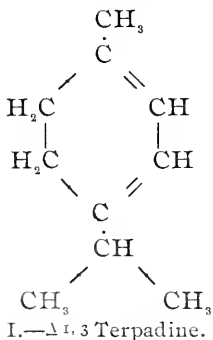
Terpin Hydrate from Limonene Monohydrochloride.

While engaged in the study of limonene and its derivatives, I made the observation that the fickle monohydrochloride of this "terpene" when in contact with water in a sealed tube in the course of time is converted into terpin hydrate, at least the appearance of the crystals as well as the transparency of the reaction seemed to justify this assertion. That it was justified I have recently determined by taking the melting-point of the crystals. When heated slowly they began to melt at 103° and were completely liquified at 116° . The contents of the tube, which had been heated considerably above the melting-point of terpin hydrate, after congealing melted completely at 103° , thus showing that it had been converted into anhydrous terpin.

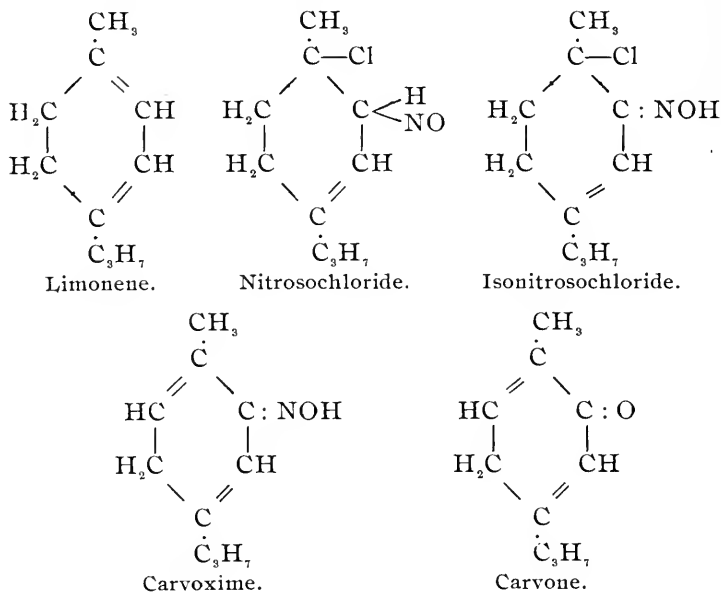
It may not be without interest to state that for more than three years the crop of crystals constantly though very slowly increased and that the monohydrochloride remained practically colorless. Then by accident the tube was broken; the oil became colored and ultimately dark brown, while at the same time the crystals were gradually redissolved by the mother-liquid. I mention this in case some one should desire to prepare terpin hydrate from limonene monohydrochloride.

On the Constitution of Limonene.

Prof. O. Wallach and Prof. A. v. Baeyer have both within the past year discussed the constitutional formula of limonene. The following formulas, which differ only with reference to the position of one of the two double bonds, have been suggested and arguments pro and con have been discussed.



The older formulas, which gave an assymmetric carbon atom to limonene on account of its optical activity were unsatisfactory because they did not admit primarily of a satisfactory explanation of the conversion of limonene into carvone. In the recent discussions this reaction seems to have been ignored entirely. It may, therefore, not be out of place to call attention to the fact that formula I. admits of a very simple explanation of this reaction. The carvone formula to which it leads is that recently suggested by v. Baeyer. This reaction, therefore, has attained a double significance. It seems to ratify v. Baeyer's first formula for limonene as well as his formula for carvone. On account of this simple explanation, expressed by the following formulas, the writer favored formula I. even before v. Baeyer suggested the same, who assigned formula II. at that time to terpinene.



These reactions are perfectly analogous to those which have been studied in connection with menthene nitrosochloride and which have lead to Δ^4 Terpene-3-one. Similar reactions are now being studied in connection with pinene nitrosochloride. In this case, however, a rearrangement of the

double, or rather para, bonds takes place and the expected ketone is converted into a phenol.¹

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Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE ACTION OF BROMINE ON METANITRANILINE.

BY H. L. WHEELER.

The action of the halogens on metanitriline has been investigated only in a hydrochloric-acid solution: Körner¹ prepared *s*-tribrommetanitriline by saturating the aniline with bromine in a dilute acid solution. Wurster and Nölting² state that they did not obtain a pure product in this manner. I have repeated the work of Körner and have found that the product formed in largest amount, by the action of bromine in a hydrochloric-acid solution, is *s*-tribrommetanitriline, even when the operation is performed in the cold and in the presence of an excess of metanitriline. Similar results were obtained when the nitriline was dissolved in concentrated sulphuric acid, one molecule of bromine added and the mixture heated to 130° in a sealed tube. Bromine in cold concentrated sulphuric acid has little action on metanitriline.

It is to be noticed that the behavior of metanitriline, under the above conditions, is perfectly analogous to that of aniline.³ It has been frequently observed that other meta substituted anilines behave like aniline where exposed to the action of the halogens. Nölting⁴ called attention to this fact, as follows "Ueberhaupt verhält sich ein bei 3 substituirtes Anilin Agentien gegenüber gerade so wie ein gar nicht substituirtes." Later this idea was further developed by Langer.⁵ He investigated the final action of chlorine and bromine on a number of substituted anilines and summarized the results in the form of the following law: "dass bei weiterer Substitution des

¹ See this JOURNAL, 17, 607 *et seq.* ² Jsb. 1875, 346.

³ Ber. d. Chem. Ges. 7, 1564.

⁴ Compare Hafner: *Ibid.* 22, 2524.

⁵ *Ibid.* 8, 1093.

⁶ Ann. Chem. (Liebig), 215, 107; Ber. d. Chem. Ges., 15, 1061, 1328.

Anilins solche Substituenten, die zur Amido gruppe die Metastellung einnehmen gar keinen bemerkbaren Einfluss ausüben und die Zahl der neu eintretenden Halogenatome nicht verringern."

It is to be noticed that these statements apply when the anilines are exposed to the final action of chlorine and bromine, since the work from which they were derived consisted in saturating the meta substituted anilines with chlorine and bromine. It has been found, however, in the case of metanitriline that these generalizations do not apply under any other than the above mentioned conditions. In other cases, not only does the nitro group in the meta position exert a decided influence on the substitution of the aniline, but it also diminishes the number of halogen atoms that the non-substituted aniline is capable of taking up. Indeed even before the publication of Langer's observations, it had been shown by Michael and Norton¹ that a nitro group in the meta position diminishes the number of iodine atoms that the aniline when not substituted is capable of taking up. They found that aniline and iodine monochloride gave *s*-triiodoaniline while under the same conditions metanitriline and iodine monochloride gave only diiodometanitriline. These authors also found that iodine monochloride does not further substitute this di derivative even at 100°.

I have found that the nitro group exerts a protective influence on the aniline in regard to further substitution by bromine.² In the case of orthobrommetanitroacetanilide this substance can be crystallized unaltered from pure bromine. On the other hand acetanilide readily forms a dibrom derivative.

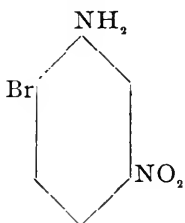
If metanitriline is brominated, using the proper quantity of bromine, in a glacial acetic-acid solution, the chief product formed is a new monobrommetanitriline, $[\text{NH}_2, \text{NO}_2, \text{Br} : 1, 3, 6]$. The entering bromine takes the ortho position to the amido group. Under similar conditions aniline gives principally tri- and dibrom anilines. Moreover the mono derivatives

¹ Ber. d. Chem. Ges., 11, 112.

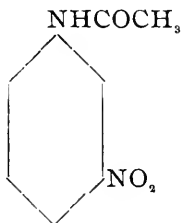
² This is most noticeable in the case of the acetyl compounds. On brominating metanitroacetanilide only parabrommetanitroacetanilide was formed and this gave no higher substitution-product with an excess of bromine.—This JOURNAL 17, 612.

formed, when the halogens act on aniline, according to Mills,¹ Kekulé² and Hofmann³ are para and not chiefly ortho derivatives. Here it is evident that the nitro group, besides protecting the aniline, also influences the further substitution in another way.

The statement that a substituent in the meta position does not influence the further substitution of the aniline is not in harmony with the interesting observation of Kehrman.⁴ This author calls attention to the fact that when disubstituted benzenes are further substituted the entering substituent generally takes the ortho position to the substituent of least molecular magnitude. This is precisely what takes place in the case of metanitriline: the free base gives orthobrommetanitriline (I), while the acetyl compound yields only parabrommetanitroacetanilide (II).



I.



II.

I have recently shown⁵ that when metanitroacetanilide is brominated the reaction takes place in two stages. In the first place a dibrom addition-product is formed; this then separates hydrobromic acid giving the so-called substitution-product. No such intermediate addition-product was observed when bromine was added to the free base. In this case *s*-tribrommetanitriline and orthobrommetanitriline hydrobromide were directly obtained.

EXPERIMENTAL PART.

Orthobrommetanitriline, ($\text{NH}_2, \text{NO}_2, \text{Br} : 1,3,6$). — This new compound is formed on adding bromide to a solution of

¹ Ann. Chem. [Liebig], **176**, 355.

² Ztschr. Chem., 1866, 687.

³ Ann. Chem. [Liebig], **67**, 61.

⁴ Ber. d. chem. Ges., **23**, 130.

⁵ This JOURNAL, **17**, 612.

metanitriline in glacial acetic acid, chloroform or benzene. The first mentioned solvent is most suitable. 1 molecule metanitriline dissolved in glacial acetic acid and 1 molecule of bromine added, either in vapor form or slowly dropped in, produces a colorless shining crystalline precipitate. This consists chiefly of the hydrobromic-acid salt of orthobrommetanitriline. After washing thoroughly with glacial acetic acid it is converted into the base by means of water and a little dilute ammonia, and this on crystallizing from alcohol is readily obtained pure. It then separates in the form of bright yellow needles melting at 139° – 140° . A bromine determination was made by the method of Carius.

0.2638 gram substance gave 0.2262 gram AgBr.

	Found.	Calculated for $C_6H_5N_2O_2Br$.
Br	36.49	36.86

This substance gave with ethyl nitrite parabromnitrobenzene and, by means of Sandmeyer's reaction, dibromnitrobenzene ($NO_2, Br, Br: 1,3,4$). The structure is therefore: $NH_2, NO_2, Br: 1,3,6$.

Orthobrommetanitriline dissolves readily in ether, chloroform, or benzene, less readily in alcohol, and difficultly in ligroin and in water. From water long hairlike golden-yellow needles separate; these have a magnificent silky lustre. This substance is readily volatile in steam; its most characteristic property is its remarkable sweet-licorice taste, which can be detected in extremely dilute solutions.

It seemed of interest to determine whether the corresponding chlorine derivative [$NH_2, NO_2, Cl: 1,3,6$] had a sweet taste. This was prepared according to the method of Claus and Stiebel.¹ After purification, by means of ligroin, which completely extracts the bitter bye-products, the chlorine derivative had the sweeter taste. This is probably due to its greater solubility.

Orthobrommetanitriline is less basic than parabrommetanitriline. Salts can be obtained by dissolving the substance in strong acids; these are decomposed by water.

The *hydrochloride*, $C_6H_5.NH_2.NO_2.Br.HCl$, crystallizes in

¹ Ber. d. chem. Ges., 20, 1379.

colorless shining scales, which are difficultly soluble in concentrated hydrochloric acid. These melt with decomposition at about 200° .

0.2919 gram substance dried over sulphuric acid gave 0.1652 gram AgCl.

	Found.	Calculated for $C_6H_3.NH_2.NO_2.Br.HCl$.
HCl	14.39	14.39

The *sulphate*, $(C_6H_3.NH_2.NO_2.Br)_2.H_2SO_4$, crystallizes in beautiful colorless, shining, extremely thin, broad plates. These readily inclose some of the strong acid mother-liquor.

0.503 gram substance dried over sulphuric acid gave 0.272 gram $BaSO_4$.

	Found.	Calculated for $[C_6H_3.NH_2.NO_2.Br]_2.H_2SO_4$.
H_2SO_4	22.7	18.4

Orthobrommetanitroacetanilide.—This was obtained by boiling the glacial acetic-acid solution of the base for a half-hour with acetyl chloride and anhydrous sodium acetate. It is readily soluble in hot alcohol, difficultly in water. It crystallizes in beautiful, colorless, silky needles melting at 180° .

0.2717 gram substance gave 0.1948 gram AgBr.

	Found.	Calculated for $C_6H_7N_2O_3Br$.
Br	30.5	30.8

s-Tribrommetanitriline, $(NH_2.Br.NO_2.Br.Br: 1,2,3,4,6)$. This substance is found in the glacial acetic-acid filtrate when metanitriline is brominated as indicated above. When this filtrate is diluted with about two volumes of water the tribromide is precipitated along with whatever resinous products have been formed. The precipitate, boiled with dilute alcohol and animal charcoal, gives, on filtering and cooling, pale yellow needles melting at 102° – 103° .

0.2928 gram substance gave 0.4412 gram AgBr.

	Found.	Calculated for $C_6H_3N_2O_2Br_3$.
Br	64.12	64.00

This compound, as already stated, was obtained by adding bromine to a hydrochloric-acid and a sulphuric-acid solution of metanitriline. The hydrochloric-acid solution as describer by Körner¹ is most suitable for its formation.

¹ *Loc. cit.*

s-Tribrommetanitriline exhibits weakly basic properties. Salts cannot be prepared in the presence of water. They are very unstable and are readily decomposed on exposure to the moisture of the air. The hydrochloride is obtained by saturating a strong benzene solution of the base with dry hydrochloric acid gas. It crystallizes in colorless needles or prisms. The formation of the sulphate was observed when a mixture of 5 grams of metanitriline, 50 grams of concentrated sulphuric acid, and 7.5 grams of bromine were heated in a sealed tube for eight hours to 120° – 130° . On cooling the tube was filled with a mass of colorless needles. These were washed with concentrated sulphuric acid and finally with ether. Qualitative tests then proved that this was the sulphuric-acid salt and not the hydrobromide. On crystallizing the sulphate from alcohol *s*-tribrommetanitriline was obtained. Ice-water precipitated more of the base from the sulphuric-acid filtrate. On account of the unstable nature of these salts they were not analyzed.

s-Tribrommetanitroacetanilide. — This compound was prepared in the same manner as given under the head of orthobrommetanitroacetanilide. On crystallizing from alcohol colorless prisms or stout crystals separated; these melted constantly at 169° . Concentrated nitric acid decomposes this substance with greater difficulty than the monobrominated aniline. A bromine determination was made according to the method of Carius, in which the substance was heated with nitric acid to 200° – 250° for several days. This gave 2 per cent. less bromine than the calculated amount. Orthobrommetanitroacetanilide on the other hand was readily and completely decomposed by this treatment.

Orthobrommetanitriline hydrobromide and *s*-tribrommetanitriline are the chief products of the action of bromine on metanitriline in a glacial acetic-acid solution. From 100 grams of metanitriline 87.5 grams of crude orthobrommetanitriline and 19 grams of tribrommetanitriline were obtained, while about 30 grams of unaltered aniline were recovered. The metanitriline was obtained after the removal of the tribromide, by adding ammonia to the diluted acetic-acid filtrate. The precipitate thus produced weighed 30.5

grams. On crystallizing from dilute alcohol it melted at 114° and was practically free from bromine. It therefore consisted chiefly of unaltered metanitraniline. The material in the mother-liquor from this amounted to only a few grams, it had a strong sweet taste and it also contained bromine. This material was probably a mixture of ortho and para monobrom derivatives with metanitraniline.

The alcoholic mother-liquor from the purification of orthobrommetanitraniline was evaporated to dryness, a little sulphuric acid was added and the whole distilled in steam. This removed the orthobrom derivative completely. The residue was filtered, dissolved in alcohol, concentrated hydrochloric acid was added and the whole evaporated to dryness. The residue was then extracted repeatedly with quite dilute hydrochloric acid, the solutions were united and precipitated with ammonia. On crystallizing the precipitate thus produced repeatedly from a mixture of benzene and ligroin it melted finally at 130° . This was probably parabrommetanitraniline. A sufficient quantity of pure material was not obtained for satisfactory identification. The residue left undissolved by the hydrochloric acid, amounted to only a few grams; it consisted of what seemed to be a mixture of the dibrommetanitranilines. Experiments undertaken to separate these were without success.

An attempt to prepare the dibrommetanitranilines, by mixing the calculated quantity of bromine with the anilides dissolved in glacial acetic acid, resulted in a proportionally larger yield of mono- and tribrommetanitranilines. 10 grams metanitraniline dissolved in 100 grams of glacial acetic acid were treated with 23.2 grams of bromine in 25 grams of glacial acetic acid. This gave 11.1 grams of crude monobrom- and 10.7 grams of tribrommetanitraniline. On crystallizing the mono derivative from alcohol, 6.4 grams of pure substance were obtained.

It is my intention to investigate the action of bromine on propylmetanitraniline or on methylethylmetanitraniline. It is hoped in this manner to obtain results which will throw more light on the action which takes place when both metanitraniline and metanitroacetanilide are brominated. The

relative molecular magnitudes of the substituents in these anilines are the same as in metanitroacetanilide, but these compounds differ from metanitroacetanilide inasmuch as the groups $-\text{N} < \begin{smallmatrix} \text{H} \\ \text{C}_3\text{H}_7 \end{smallmatrix}$ and $-\text{N} < \begin{smallmatrix} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{smallmatrix}$ are more basic than the group $-\text{N} < \begin{smallmatrix} \text{H} \\ \text{COCH}_3 \end{smallmatrix}$. These compounds, like metanitroacetanilide, should give principally parabrom derivatives, if the process of bromination in each case is the same or if the position of the entering bromine atom is determined by the relative molecular magnitudes of the substituents. If on the other hand the basicity determines the position of the bromine atom, ortho derivatives would be formed, as in the case of the action of bromine on metanitriline.

July, 1895.

A NEW REAGENT FOR BROMINE AND IODINE. PRELIMINARY NOTICE CONCERNING THE HALOGEN DERIVATIVES OF THE SULPHONAMIDES.

BY J. H. KASTLE.

Some months ago while working with *p*-chlorbenzenesulphonamide, a new bromine derivative of this substance was obtained by treating a caustic-soda solution of the amide with bromine water. The substance thus obtained was crystalline, yellow in color, possessed a slight odor of bromine and on analysis gave the following numbers:

	Calculated for $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{SO}_2\text{NH}_2\text{Br}_2 \\ \text{Cl}(p) \end{smallmatrix}$	
Br	45.53	45.51
N	3.80	3.98
S	9.70	9.10

An examination of the literature showed that no halogen derivative of the sulphonamides had ever been described. Several such derivatives of the carbonic amides, however, are well known, and by analogy the compound above mentioned ought probably to be regarded as of this nature: $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{SO}_2\text{N} \cdot \text{Br}_2 \\ \text{Cl}(p) \end{smallmatrix}$, *i. e.*, as a dibrom substitution-product of the *p*-chlorbenzenesulphonamide in which the two bromine

atoms have replaced the two hydrogen atoms in the amide portion of the compound. That such really is the case, seems at the present writing to be open to doubt. Even in the case of similar derivatives among the carbonic amides, this structure seems open to question, and yet, apparently without much question, such a structure has been commonly assigned. For example, these formulas have been used repeatedly :

CH_3CONHBr ; $\text{CH}_3\text{CONBr}_2$; $\text{C}_6\text{H}_5\text{CONHCl}$; $\text{C}_6\text{H}_5\text{CONHBr}$;
 $\begin{array}{l} \text{CH}_2\text{CO} \\ \text{CH}_2\text{CO} \end{array} > \text{N.Cl}$; in spite of the fact that in no instance, save possibly one, has any reaction of which they are capable seemed to show that the halogen atoms occupy the place of the hydrogen in the amide. In fact one of the most characteristic reactions of this class of bodies is that with various reagents—acids, alkalies, etc.—they yield the corresponding amides.

In his efforts to synthesize higher compounds of nitrogen through the aid of these derivatives Bender¹ failed, as did also later Linebarger,² "benzamide being the only crystallizable compound obtained." I quote the latter's words concerning his results with the bromine derivative of benzamide, the formula of which is given as $\text{C}_6\text{H}_5\text{CONHBr}$.

In view therefore of the unsatisfactory condition of our knowledge concerning the nature of the halogen derivatives of acid amides, it was thought advisable to make a thorough study of this subject. The halogen derivatives of the sulphonamides being chosen as "the substances best suited to this study in consequence of the ease with which they can be obtained in beautifully crystalline condition. A number of the di-halogen derivatives of several sulphonamides have been prepared, two of which, the dibrom and the dichlor derivatives of benzene sulphonamide are of remarkable beauty. The conduct of these substances towards a good many simple reagents has been studied. As in the case of the halogen derivatives of benzamide the amide itself seems to be the end-product of nearly all of these reactions, and yet the data at hand at present are hardly sufficient to enable one to reach a satisfactory conclusion concerning the structure of these substances.

¹ Ber. d. chem. Ges., 19, 2274.

² Linebarger : This JOURNAL, 16, 216.

Among the other transformations of which these derivatives are capable may be mentioned one which is most peculiar and interesting, and, so far as I am aware, entirely without a parallel among chemical reactions.

It is this: when the dichlor derivative of the benzenesulphonamide is heated to about 170° , it decomposes with evolution of chlorine, nitrogen and hydrochloric acid and gives almost the theoretical quantity of benzenesulphon chloride, a decomposition which is remarkable in many respects.

The Dichlor Derivative of Benzene Sulphonamide as a Reagent for Bromine and Iodine.

Among the other reactions of which it is capable, it was found that the dichlor derivative of benzene sulphonamide decomposes metallic bromides and iodides with the formation of the metallic chlorides and the corresponding brom and iodo derivatives of the amide; and it was further observed that when this decomposition was effected in the presence of carbon bisulphide or chloroform the latter solvents were colored yellow and violet just as they are with bromine and iodine.

The use of chlorine-water as a reagent in testing for bromine and iodine, is not altogether free from objections, not the least of which is, that at the moment when most needed a quantity of this reagent carefully prepared and placed in a dark closet will be found to have altered so that it is no longer a solution of free chlorine but one of hydrochloric acid, and hence of no use for this purpose.

The uncertain character of a bottle of chlorine-water has doubtless been the matter of an unhappy experience in the lives of most chemists. It was therefore deemed expedient to test this new compound as a reagent for bromine and iodine, the specimen used in these experiments being one which had been kept in this laboratory during the summer months in a loosely stoppered bottle.

The tests were made with the following solutions with the following results:

SOLUTIONS.

Solution I., containing 127 parts of iodine per million; made by dissolving 0.0166 gram potassium iodide in 100 cc. of water.

Solution II., containing 80 parts of bromine per million; made by dissolving 0.0119 gram potassium bromide in 100 cc. of water.

Solution III., containing 12.7 parts of iodine per million; made by making 10 cc. of Solution I. up to 100 cc. with water.

Solution IV., containing 8000 parts of bromine per million. Made by dissolving 1.19 grams of potassium bromide in 100 cc. of water.

No. of experiment.	Amount in cc. used. Solution.				Water.	Reaction for iodine.	Reaction for bromine.
	I.	II.	III.	IV.			
1	5.0	Very decided.
2	1.0	4.0	Good.
3	0.5	6.0	Perfectly distinct.
4	0.2	9.8	Distinct.
5	0.5	10.0	Very distinct.	Good.
6	0.4	9.8	Distinct.	Distinct.
7	5.0	Good.
8	1.0	Slight but distinct.
9	...	5.0	5.0	Distinct.
10	5.0	1.0	Distinct.	Distinct.
11	0.5	4.5	Slight but distinct.
12	4.5	0.5	Distinct.
13	2.0	5.0	Perfectly dist'ct.	Excellent
14	1.0	0.5	Distinct.
15	1.0	5.0	Perfectly dist'ct.	Excellent

According to these results it is possible by the proper use of this new reagent to recognize 0.0000127 gram of iodine in the presence of 0.0400 gram of bromine; or 0.00000635 gram of iodine in the presence of 0.00036 gram of bromine.

My friend, Dr. A. M. Peter, chemist of the Agricultural Experiment Station here, was good enough to repeat some of the above experiments for me with results altogether similar to those above given. It is his opinion that as a reagent for iodine, the dichlor derivative of benzene sulphonamide is more satisfactory than potassium nitrite.

In the light of these results there can be no question as to the delicacy of this new compound as a reagent for bromine and iodine. I therefore propose its use for this purpose, and give the following method for its preparation: Benzene sulphonamide is dissolved in the smallest possible quantity of a

1 : 10 solution of caustic soda, and into this solution there is conducted a rapid current of chlorine. Under these conditions a white precipitate is produced by the chlorine, the first portions of which contain considerable quantities of the unchanged amide. This should be filtered out and the filtrate again treated with the gas. The second precipitate thus produced consists chiefly, if not entirely, of the dichlor derivative of the amide. It is filtered out of the solution and partly purified by heating with water and decanting. Under these circumstances the dichlor derivative, melting as it does at 70° , and being nearly if not entirely insoluble even in hot water, is separated from any of the original amide with which it is admixed as a light yellow oil, which solidifies when poured into cold water. In appearance and in many of its physical properties it resembles a solid acid chloride. It may be further purified by dissolving in absolute alcohol and adding a small quantity of water, which latter substance precipitates it in the form of white, lustrous, pearly plates.

In using the substance in testing for bromine and iodine it may be added either in the solid state or in solution in carbon bisulphide; indeed in testing for very minute quantities of iodine it is preferable to use the carbon-bisulphide solution for the reason that smaller quantities of the reagent can thus be added to the solution containing the bromine or iodine. In this connection it must be borne in mind of course that in testing for very minute quantities of iodine it is necessary to add correspondingly small quantities of the reagent for the reason that, like chlorine, it reacts with the iodine set free to form the colorless iodine trichloride, and hence if care be not exercised, very small quantities of iodine may escape detection.

STATE COLLEGE OF KENTUCKY, *October, 1895.*

REVIEWS.

THE DISSOCIATION OF ELECTROLYTES AS DETERMINED BY SOLUBILITY-EXPERIMENTS.

Several papers have appeared during the past few years on the determination of the dissociation of electrolytes by means of solubility-experiments, and as the problem is now satisfactorily solved, it seems desirable to review the different papers

that have been published on this important subject. The first of these was published by Nernst,¹ and was on the mutual influence of salts on their solubility. He begins by showing how to calculate the amount of work that would have to be done against osmotic pressure in order to dissolve, at a fixed temperature, a gram-molecule of any substance in a solvent which is already saturated and constantly kept so, by proper addition of solvent, with the substance in question. The conclusion is that, where chemical action is absent, this work is independent of the nature, both of the dissolving substance and of the solvent. This is but the application of a well-known gas law to solutions, and at once suggests the application of other gas laws. Among these is the law that the amount of gas which a given space will contain, at ordinary pressure, is nearly independent of the presence of other gases which are neutral with respect to the one under consideration, and it is found that the same statement is applicable to solutions. Another gas law, of importance in this connection, is embodied in the statement that if any enclosed space be saturated with a gas which is known to dissociate, and if an additional amount of one of the dissociated parts be added, a corresponding amount of the original non-dissociated substance will separate out, while no change will take place on the addition of a neutral foreign gas. Thus, if a given space be saturated with ammonium chloride, which is known to dissociate into ammonia and hydrochloric acid, ammonium chloride will be deposited on the addition of either ammonia or hydrochloric acid, but no change will take place on the addition of a neutral gas, *e. g.*, nitrogen. This law was known to hold at least qualitatively in the case of solutions also, but Nernst tested it quantitatively by adding to saturated solutions of silver acetate known amounts of sodium acetate in one case and silver nitrate in another. Silver acetate was always precipitated from the solution to an extent corresponding to the amount of the sodium acetate or silver nitrate added. The relation between the quantities of the salts in solution was in fair accord with the formula, suggested by the above gas laws, $m(m+x) = m_o^2$, where m_o is the number of gram-molecules per liter of the silver acetate in a saturated solution; x that of the sodium acetate or silver nitrate added; and m that of the silver acetate in solution after the addition of the silver nitrate or sodium acetate. The above formula assumes complete dissociation, an assumption which lowering of the freezing-point and conductivity-experiments show is not correct except for very dilute solutions. By allowing for this we obtain the corrected for-

¹ Ztschr. phys. Chem., 4, 372.

mula $m\alpha(m\alpha + x\alpha') = m_0^2\alpha_0^2$, where α , α' and α_0 are respectively the activity-coefficients, or percentages of dissociation, of m , x and m_0 . This equation does not enable us to determine m in terms of known quantities, but as conductivity-experiments show that certain salts—potassium chloride, potassium bromide, sodium chloride, sodium acetate and others—dissociate to nearly the same extent in solutions of equal concentration, it is therefore natural to suppose that in such cases by taking

$\frac{m}{m+x}$ cc. of the one salt solution and $\frac{x}{m+x}$ cc. of the other, where x and m are their respective concentrations, we

should have $\alpha = \alpha'$ and consequently $m = -\frac{x}{2} + \sqrt{m_0 \left(\frac{\alpha_0}{\alpha}\right)^2 + \frac{x^2}{4}}$.

This makes possible the calculation of m when α is known, or the reverse, since the other terms are all known. The few experiments described by Nernst agree well with this formula. Many persons had previously worked on the mutual influence of salts on their solubility, but without reaching any general law; probably because in most cases they worked with easily soluble salts which possibly modify the solvent and which give osmotic pressures amounting to hundreds of atmospheres—pressures at which ordinary gas laws do not hold.

The next paper on this subject is by Noyes,² who subjected Nernst's solubility-law to a number of careful tests and found it to hold in the main very well, though certain discrepancies between the values of m , as calculated by the formula and those found by experiment, lead him to question the values of α given by conductivity. He therefore undertook to determine the values of α in certain cases by means of solubility, which is possible by Nernst's formula as well as by the following equation, given by the law of mass-action, $m(1-\alpha) = m_0(1-\alpha_0)$. The former is used, which, of course, is assuming that the dissociations of the two salts concerned are the same, and Noyes therefore, apparently with good reason, assumed that under similar conditions, thallium salts, with which he worked, are dissociated to the same extent as the salts of the alkali metals. He was thus enabled to calculate for various concentrations the dissociation-constant, which for binary electrolytes is equal, from the law of mass action, to $\frac{1-\alpha}{n\alpha^2}$ where n is the number of gram-molecules per liter in

solution. This he found by his experiments to be nearly a constant, which theory indicates it should be, even in places where conductivity gave it widely differing values, and so he

² Ztschr. phys. Chem., 6, 241.

concluded that dissociation can be determined more accurately by means of solubility-experiments than by conductivity.

This line of work was continued by Noyes¹ and the results were published in another paper which is chiefly a report of a large number of experimental determinations of dissociation by means of solubility, which method he still thought more reliable than that of conductivity.

Arrhenius² is next to take this matter up. He objects to the views of Noyes as they forced him to conclude that water is dissociated enough to play an important part in the conductivity of electrolytes, which is contrary to Hittorf's³ investigations. Arrhenius therefore carried out a series of solubility-experiments himself, and from them calculated the dissociation on the assumptions that the non-dissociated part of the salt in solution is constant, at any given temperature, and independent of the presence of any neutral substance in the solution, and that the law of mass-action holds for electrolytes in solution—the law which conductivity renders doubtful for easily soluble salts, strong acids and strong bases, but which seems supported by Noyes' work. The values of the so-called dissociation-constant, $\frac{1-a}{na^2}$, obtained in this way by Arrhenius, for different concentrations of a given salt in presence of another, differ widely and seem to depend in some way on the solubility of the second salt. Consequently Arrhenius claims that his second assumption, law of mass-action, does not apply to strongly dissociated electrolytes. The paper, however, is not conclusive, as Noyes states in a subsequent article, from the fact that it is assumed without sufficient reason that the dissociations of the salts which are used to influence each other's solubility are the same.

The next paper bearing on this important subject is by Jones⁴ who made a large number of careful determinations with most excellent apparatus, of the lowering of the freezing-point of very dilute salt-solutions. Several different salts were used, and their dissociation as calculated from his experiments, agree closely with those obtained by conductivity, and, consequently, differ from those found by Noyes.

For the sake of completeness it is necessary to state that Noyes⁵ wrote a short reply to Arrhenius in which he calls attention to the latter's unwarranted assumptions, but admits that he is convinced that water is not dissociated sufficiently to account for the difference between theoretical and observed values of conductivity.

¹ Ztschr. phys. Chem., 6, 241.

² *Ibid.* 11, 391.

³ Ann. der Phys. Pogg., 103, 13.

⁴ Ztschr. phys. Chem., 11, 529.

⁵ *Ibid.* 12, 162.

The final and very satisfactory paper is by Noyes and Abbot.¹ In this, attention is called to the fact that the error which led to the discrepancies between results given in Noyes' earlier communications and those found by conductivity, was his assumption that thallous chloride is dissociated the same as the chlorides of the alkali metals. Neither this nor any other assumption is now made, but everything based on experiment as follows: Let m_0 and m'_0 be the solubilities of two salts in pure water, m and m' their respective solubilities when both are present in excess, α_0 , α'_0 , α and α' the corresponding values of dissociation. We then have at once, for binary electrolytes, $m_0(1-\alpha_0)=m(1-\alpha)$, $m'_0(1-\alpha'_0)=m'(1-\alpha')$, $m_0^2\alpha_0^2=m\alpha(m\alpha+m'\alpha')$ and $m'^2_0\alpha'^2_0=m'\alpha'(m\alpha+m'\alpha')$. These four equations involving only four unknowns, α_0 , α'_0 , α and α' enable us to find the value of any one of them in terms of known quantities. Values of dissociation determined in this way agree almost exactly with those found by conductivity and lowering of the freezing-point, thus giving further support to Nernst's solution law, and also showing that the so-called dissociation-constant—ratio of undissociated molecules in solution to the product of the ions—is really not a constant but a variable that increases with increase of dilution, though why this should be so no one has yet satisfactorily answered.

W. J. HUMPHREYS.

¹ *Ibid.*, 16, 125.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XX.—ON THE COMPOSITION OF THE OHIO AND CANADIAN SULPHUR PETROLEUMS.¹

BY CHARLES F. MABERY.

Notwithstanding the great number of investigations that have been undertaken on petroleum from different countries, our knowledge of their composition, especially of the portions with high boiling-points, is still incomplete. What is known concerning American petroleum is based chiefly on the results of investigations which were carried on thirty years ago, before the discovery of several series of organic compounds, since shown to be contained in certain petroleum. With these facts in view, and having found in the study of the sulphur compounds from Ohio and Canadian petroleum that these oils are in certain respects peculiar in their composition, I have undertaken a comprehensive examination of them with reference to the different series of products which they may be found to contain. The study of Ohio petroleum seemed especially inviting on account of its origin in the Trenton limestone, a new horizon for a prolific oil supply, and its association with animal remains in the oldest geological formations of the continent. A similar interest attaches to the Canadian

¹ Presented to the American Academy of Arts and Sciences, October, 1894. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Chemical Research.

petroleum from the Corniferous limestone, which has yielded since 1862 enormous quantities of oil within the limited areas, less than thirty square miles, at Petrolia and Oil Springs. From the information already acquired concerning the nature of the sulphur petroleums, they seem to possess, beside their distinctive characteristics due to sulphur constituents, qualities of other petroleums which differ essentially in their composition.

In the earlier attempts to ascertain the constituents of petroleum, the methods then employed for fractional distillation were so inadequate that very little was accomplished. In 1862 the first systematic examination of American petroleum was undertaken by Pelouze and Cahours,¹ who showed the presence of the series of hydrocarbons C_nH_{2n+2} , beginning with butane. On account of a want of suitable apparatus for fractional distillation, their results lacked precision, and the questionable assumption was based upon them that petroleum is composed principally, including the heavier oils and paraffin, of the homologues of marsh gas. In accordance with the suggestion of Watts, these bodies were called the paraffin hydrocarbons, and as such they have since been known in chemical literature. Having obtained from coal-oil a series of hydrocarbons corresponding to certain members of the series discovered by Pelouze and Cahours, Schorlemmer² submitted the more volatile portions of American petroleum to distillation, and succeeded in separating hydrocarbons that had not been recognized by Pelouze and Cahours. In a more thorough and carefully conducted examination of Pennsylvania petroleum, carried on contemporaneously with the investigations of the chemists mentioned above, by means of an efficient fractional condenser devised especially for this and other similar investigations, C. M. Warren³ avoided the errors of other experimenters and established beyond question the presence in Pennsylvania oil of two series of hydrocarbons, each with an homologous difference in boiling-points for CH_2 of 30° , and each member of one series differing in boiling-point from the isomeric member of the other series by a little less

¹ *Compt. Rend.*, **54**, 1241; **56**, 505; **57**, 62.

² *J. Chem. Soc.*, **15**, 419, (1862).

³ *Mem. Amer. Acad. (N. S.)* **9**, 135; *Proc. Amer. Acad.*, **27**, 56.

than 8° . One of the series $C_n H_{2n+2}$ identified by Warren terminates at $127^{\circ}.6$, the other at 150° , the fractions of higher boiling-points containing members of the series $C_n H_{2n}$. The assumption of Pelouze and Cahours that the fractions with higher boiling-points have the composition represented by the general formula $C_n H_{2n+2}$ was shown to be erroneous by the results of Warren, which excluded members of this series above 151° .

The presence of aromatic hydrocarbons in American petroleum was first recognized by Schorlemmer in 1865. Pelouze and Cahours had previously stated that American petroleum contained no aromatic hydrocarbons, but Schorlemmer collected a distillate from Canadian petroleum below 150° , and upon treating it with nitric acid and reducing with tin and hydrochloric acid, after distillation he obtained an oil with an odor of aniline that gave, with bleaching powder, the rosaniline reaction. The portion distilling between 150° and 170° gave a mixture of solid and liquid nitro-products, and the solid portion proved to be trinitrocumol. Benzol and its homologues were also found by Schorlemmer in Pennsylvania petroleum, in Galician petroleum by Freund¹ and others, and in Hanover petroleum by Bussenius and Einstuck.² In Galician petroleum Pawlewski³ found two per cent. of aromatic hydrocarbons, chiefly benzol and paraxylol, the latter never having previously been recognized in any petroleum. In the fraction 170° – 190° from American kerosene, Engler⁴ discovered pseudocumol and mesitylene by the formation of nitro-compounds, and calculating the weight of crude oil corresponding to the weight of kerosene taken, it was estimated that these constituents are contained in crude Pennsylvania oil to the extent of 0.2 per cent. These hydrocarbons were also found in German, Galician, Italian, and Russian petroleum, in the latter to the extent of 0.1 per cent. According to the results of Beilstein and Kurbatoff,⁵ the petroleum of the Central Caucasus has an essentially different composition from that of the deposits on the coast of the Caspian Sea. Oil obtained from the region of Zarskige Kolodzy, in the precinct of

¹ Ann. Chem. (Liebig) **115**, 19.

² *Ibid.*, **113**, 151.

³ Ber. d. Chem. Ges., **18**, 1915.

⁴ *Ibid.*, **18**, 2234.

⁵ *Ibid.*, **13**, 1818; **14**, 1620.

Tiflis in the Central Caucasus, proved to contain small amounts of benzol and toluol, but to consist principally, like the Pennsylvania petroleum, of the series $C_n H_{2n+2}$. Pentane, hexane, and heptane were identified. The oil from Baku on the coast contains the series $C_n H_{2n+2}$ in smaller quantity, and Beilstein and Kurbatoff found no trace of the aromatic hydrocarbons $C_n H_{2n-6}$, but the principal constituents are members of the series $C_n H_{2n}$. In Pennsylvania petroleum, Beilstein and Kurbatoff¹ recognized hexahydroisoxylol. In the fraction 95°–100° the same chemists detected the presence of a body containing less hydrogen than is required for the series $C_n H_{2n+2}$. Crude American heptane, when treated with nitric acid, gave a nitro-product corresponding to the formula $C_7H_{15}NO_2$. Nearly coincident with the researches of Beilstein and Kurbatoff, Schützenberger and Jonine² identified in the petroleum of Baku, hexahydrobenzol and hexahydrotoluol.

In their classic researches on the composition of the Caucasus petroleum, Markownikoff and Ogloblin³ showed the presence in the oil from Baku, of benzol, toluol, isoxylol, pseudocumol, mesitylene, isodurool, durool, and higher hydrocarbons of the composition $C_{11}H_{14}$, $C_{12}H_{14}$, $C_{11}H_{12}$, and $C_{13}H_{14}$, and others, possibly homologues of styrol and phenylacetylene. Contrary to the experience of others, Markownikoff and Ogloblin found the naphtha from the Balachany plain on the Apscheron peninsula very rich in aromatic hydrocarbons; in the oil from the Central Caucasus, naphthenes were found to the extent of 80 per cent., and the aromatic hydrocarbons $C_n H_{2n-6}$ to the extent of 10 per cent. At first Markownikoff looked upon the naphthenes as isomeric with the hexahydrocompounds, but later Markownikoff and Spady⁴ appear to accept the identity of octonaphtene and hexahydroisoxylol.⁵ As members of the naphtene series $C_n H_{2n}$, Markownikoff and Ogloblin identified hexahydromesitylene and the higher homologues between C_9H_{18} and $C_{15}H_{30}$. In petroleum from Boryslaw in Galicia, beside benzol, toluol, isoxylol, and

¹ Ber. d. Chem. Ges., **13**, 2028.

² Compt. Rend., **91**, 823.

³ Ann. chim. phys., [6], 372.

⁴ Ber. d. chem. Ges., **20**, 1850.

⁵ In the *Berichte* (No. 7, April, 1895), recently received, the synthesis of 1-3-dimethylhexamethylene, C_8H_{16} (CH_3)₂ is described by Zelinsky, and it is shown to be identical with the octonaphtene of Markownikoff, or hexahydroisoxylol.

mesitylene, Lachowicz¹ found of the hexahydro series only hexahydroisoxylol.

The presence of unsaturated hydrocarbons $C_{2n}H_n$ in American petroleum was not mentioned in the early publications of Pelouze and Cahours, nor were they referred to by Schorlemmer. Warren² separated from Pennsylvania petroleum, rutylylene, $C_{10}H_{20}$, boiling-point $174^{\circ}.9$; margarylene, $C_{11}H_{22}$, boiling-point $195^{\circ}.8$; and laurylene, $C_{12}H_{24}$, boiling-point $216^{\circ}.2$. In an examination of a hydrocarbon naphtha obtained as a product of the destructive distillation of a lime soap prepared from menhaden oil, Warren and Storer³ discovered the series $C_n H_{2n+2}$, beginning with C_5H_{12} ; members of the aromatic series, including benzol, toluol, xylol, and isocumol; and a series of the general formula $C_n H_{2n}$, as follows; rutylylene, $C_{10}H_{20}$; margarylene, $C_{11}H_{22}$; laurylene, $C_{12}H_{24}$; identical with the hydrocarbons previously separated by Warren from Pennsylvania petroleum. Warren and Storer also submitted Rangoon petroleum to prolonged distillation, and they succeeded in proving the presence in this oil of rutylylene, margarylene, laurylene, cocinylylene, and naphthalene.

As early as 1842, Pelletier and Walther separated a hydrocarbon from the "steinöl" of Amiano boiling at $80-88^{\circ}$, to which they assigned the formula C_7H_{14} . A similar product with the properties of heptylene was obtained by Mabery and Smith⁴ as one of the products in the sulphuric-acid extract from the refining of Ohio burning-oil distillate.

More recently Engler⁵ subjected menhaden oil to distillation under a pressure of ten atmospheres, and from the distillates thus obtained hydrocarbons were separated which proved to be identical with those contained in natural petroleum. These products included the light constituents of gasoline, the hydrocarbons of which burning-oil is composed, the heavy oils, and paraffin. Engler, therefore, believes in the origin of petroleum from the decomposition of animal remains. The hydrocarbons distilling above 160° , referred by Pelouze and Cahours to the series $C_n H_{2n+2}$, may really be

¹ Ann. Chem. (Liebig), **220**, 187.

² Proc. Am. Acad., **27**, 56; communicated May 12, 1868.

³ Mem. Amer. Acad. (N. S.), **9**, 177.

⁴ Proc. Am. Acad., **25**, 222.

⁵ Ber. d. chem. Ges., **21**, 1816.

naphthenes or similar bodies. In most petroleum most recently examined, it is believed that the unsaturated hydrocarbons are not present in the crude oil, but when found in the products of distillation have resulted from decomposition. Beilstein and Kurbatoff stated that the series $C_n H_{2n}$ in the Caucasus petroleum does not consist of the homologues of ethylene. In the lower fractions of Galician oil, Lachowicz obtained no reaction with bromine even after long standing. Above 200° the ready absorption of bromine indicated the presence of unsaturated hydrocarbons; but it was attributed to decomposition. On the other hand, Engler¹ found that petroleums from Pechelbronn (Alsace), Oelheim (Hanover), Tegernsee, Pennsylvania, Galicia, and Baku contain members of the series $C_n H_{2n+2}$ and $C_n H_{2n}$, both unsaturated hydrocarbons and naphthenes. Engler asserts that all petroleums have the same composition, differing only in the proportions of their constituents. Markownikoff and Ogloblin² suggest the presence of unsaturated aromatic hydrocarbons in the oil from Baku.

Most analyses of crude petroleum have fallen short of 100 per cent., and the deficiency has been attributed to the presence of oxygen. In ascertaining the composition of oils from different districts, St. Claire Deville³ showed that the percentage of oxygen varies between 2.1 per cent. in the Canadian petroleum and 5.6 per cent. in the oil from Zante. In 1874, Hell and Medinger⁴ attempted to separate acids from crude petroleum by agitating it with a solution of sodic hydrate and precipitating with sulphuric acid. The oil which separated was distilled and converted into a methyl ether. By saponification of this ether an acid was obtained to which was assigned provisionally the formula $C_{11}H_{20}O_2$. From the sodic hydrate solution used in the refining of Baku oil, by the addition of sulphuric acid, Aschan⁵ separated a mixture of acids, and, taking advantage of a difference in solubility of their salts, he obtained one acid, $C_8H_{14}O_2$, distilling at $237-239^\circ$, and another, $C_9H_{16}O_2$, that distilled at $251-253^\circ$. The first acid, called by Aschan octonaphthenecarboxylic acid, by dis-

¹ Ztschr. angew. Chem., 1888, p. 73.

² Ber. d. chem. Ges., 16, 1873.

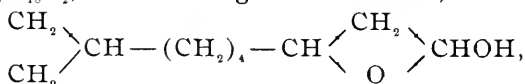
³ Compt. rend., 66, 442; 68, 485.

⁴ Ber. d. chem. Ges., 7, 1216.

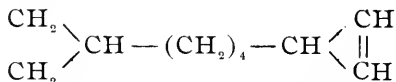
⁵ *Ibid*, 23, 867; 24, 1864, 2710; 25, 3661.

tillation with hydriodic acid, was converted into hexahydro-isoxylol.

The oxygen compounds in petroleum were considered by Zaloziecki¹ to be lacto-alcohols which are oxidized to acids by contact with air. By the same method which was followed by Hell and Medinger, and Aschan, Zaloziecki obtained an acid, $C_{10}H_{18}O_2$, to which he gave the formula,



and to the hydrocarbon obtained by distillation with hydriodic acid he gave the formula,



Engler looks upon these acids as formed by oxidation of other constituents of the crude oil. According to the results of Markownikoff and Ogloblin,² the fraction 75–85° from Caucasus oil contains 0.76 per cent. of oxygen compounds, and the fraction 220–230°, 5.21 per cent. These oxygen compounds are in part acid, in part neutral, and in part phenol. The acids $C_{10}H_{19}COOH$ and $C_{11}H_{21}COOH$ were obtained as colorless oils; Markownikoff³ and Ogloblin regarded these substances as naphtenecarboxylic acids.

Most petroleums have been shown by analysis to contain nitrogen, usually in minute quantities. In distillates from Pennsylvania oil, Beilby⁴ found 0.08 per cent. in the residuum or tar, and 0.375 per cent. in the coke. Since the tar was one-tenth of the crude oil, the latter contained 0.008 per cent. of nitrogen. In crude Russian oil Beilby found 0.05 per cent. Peckham⁵ found in West Virginia oil 0.54 per cent., in Mecca oil, 0.23 per cent., and in California oil, 0.56–1.1 per cent. of nitrogen. In Egyptian oil, Kast and Kunkler⁶ reported 0.3 per cent. of nitrogen, 1.21 per cent. of sulphur, and 0.92 per cent. of oxygen. Weller⁷ detected certain alkaloid bases in paraffin oil, and Bandrowski⁸ described a thick, transparent

¹ Ber. d. chem. Ges., **24**, 796, 1808.

² Ann. chim. phys., [6], **2**, 372.

³ Ber. d. chem. Ges., **16**, 1873.

⁴ J. Soc. Chem. Ind., 1891, p. 120.

⁵ Geological Survey of California, Appendix to Vol. **40**, 89.

⁶ Chem. Centrbl., 1890, p. 932.

⁷ Ber. d. chem. Ges., **20**, 2097.

⁸ Monatsh. Chem., **8**, 224.

liquid solidifying at 20° , which he obtained by agitating Galician oil during several weeks with sulphuric acid. This substance gave a platinum salt containing 19.7 per cent of platinum. Upon neutralizing a sulphuric acid extract obtained in refining with calcic hydrate and distilling with steam, Zaloziecki¹ obtained an oil containing nitrogen that formed a platosochloride whose percentage-composition corresponded with that of tetrahydrocoridine $(C_{10}H_{19}NCl)_2PtCl_2$, or to the formula $(C_{10}H_{21}NCl)_2PtCl_2$; another insoluble platoso compound was shown by analysis to have the composition represented either by the formula $(C_{10}H_{15}NCl)_2PtCl_2$ or $(C_{10}H_{17}NCl)_2PtCl_2$.

Several hydrocarbons have been described as occurring in the less volatile portions of American petroleum. Hemilian² obtained from the high boiling fractions "petrocene," a crystalline body melting above 300° . To this substance was assigned the formula $C_{32}H_{22}$. Prunier and David³ stated that they had obtained evidence of the presence in refinery residues of anthracene, chrysene, pyrene, phenanthrene, chrysogene, retene, benzerythrene, fluoanthrene, parachrysene, paranthracene, an isomeric acenaphthylene, besides different paraffins and stilbene. In the "petrocene" and "carbopetrocene" prepared from the tarry residue of petroleum, Prunier and David identified compounds, the former melting at $160-190^{\circ}$, the latter at $200-238^{\circ}$, and also thallene melting at 110° . They attributed the green fluorescence in petroleum to the presence of quinones. Inasmuch as these products were obtained from the distillation of tar in coking, evidently no inference is permissible concerning their presence in the crude oil. From "petrocene," Sadtler and McCarter⁴ separated two hydrocarbons, one of which melted at 280° and the other at 178° . From these hydrocarbons the quinones were prepared and from one an alizarin.

In undertaking an examination of the Ohio and Canadian sulphur oils with the advantage of former experience in studying the sulphur constituents, it was evidently necessary to conduct the distillations with all possible precautions to

¹ Monatsch. Chem., **13**, 498.

² Ber. d. chem. Ges., **9**, 1604.

³ Bull. Soc. chim. (Paris) [2], **31**, 158. ⁴ This JOURNAL, **1**, 30.

avoid decomposition. The tendency of the sulphur oils to decomposition by heat is due as much at least to the action of air on the hot oil as to the increased temperature. Markownikoff and Ogloblin attributed the decomposition in the distillation of the Russian oil to polymerization of the unsaturated compounds, and perhaps also to the polymerization of certain aromatic compounds, such as phenylacetylene, and they found that coloration of distillates on standing was less marked when the oxygen compounds had been removed. This tendency towards polymerization in unsaturated hydrocarbons separated from sulphuric-acid solutions was observed by me,¹ and it will receive further attention. It was therefore deemed advisable to carry on all distillations from the crude oils, instead of relying upon refinery products, except only the most volatile distillates, and the advantage gained has been apparent in subsidiary distillations of refinery-oils which had been subjected to the decomposition incident to refinery-distillation. Longer time is then necessary for separations, and the odor of decomposition is retained indefinitely during subsequent distillations. Certain constituents of sulphur petroleums are even more unstable than the sulphides, as shown by the rapid coloration of the oils when distilled, even after removal of the sulphides by mercuric chloride. Nevertheless, in the separation of constituents requiring larger quantities of distillates than can conveniently be collected *in vacuo*, since only porcelain or earthenware stills are admissible on account of the decomposition in metallic stills, it may be necessary to depend to a limited extent upon refinery distillates.

After the first distillation of the crude oils *in vacuo*, distillation of the portion collected below 150° was continued under atmospheric pressure, since it occasioned no appreciable decomposition. Under the diminished pressure some loss of the constituents with low boiling-points could not be avoided; but this was not important, since refinery-distillates could be utilized for the separation of the volatile hydrocarbons. Distillation of considerable quantities of oil *in vacuo* presented certain difficulties. Neither glass nor metallic stills were suitable, and no American earthenware stills could be pro-

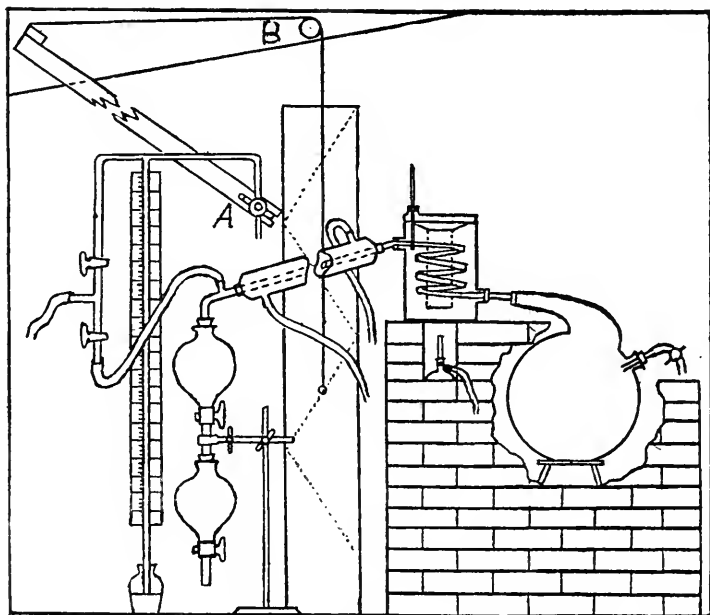
¹ This JOURNAL, 16, 92.

cured that would support a vacuum on account of porosity from imperfect molding and glazing. Some of the English earthenware has supported a vacuum, but the ideal stills for such work, or for any distillations in large quantities, when metals cannot be employed, are those manufactured in the Royal Berlin Porcelain Factory. We have had a three-gallon porcelain still and several others of smaller capacity in operation almost continuously during several months with apparently no deterioration. When these stills are enclosed within a brick chamber, the temperature of distillation may, without difficulty, be carried above 350° by means of large laboratory burners. Another serious obstacle immediately presented itself in the porosity of common corks, which alone could be used for connections. After much labor it was found that tight joints could be secured by means of a rubber lute made by dissolving gum rubber in very light gasoline. Thin films of this lute drawn by the inward pressure into the joints and imperfections in the corks, after several applications, formed sufficiently close connections. Any other than the lightest gasoline as a solvent leaves a sticky film that is unpleasant to manipulate.

An important feature in prolonged fractional distillations *in vacuo* is a simple and convenient means for maintaining, without too close attention, a constant tension within the still. Air must not come in contact with the hot oil or vapor, and it would require too large quantities of an inert gas. An expedient suggested itself in the fact that occasionally small leaks held the manometer column stationary at whatever height it happened to stand. It therefore seemed possible to graduate leaks apart from the still in such a manner that the tension could be held constant for some time at any desired point.

The accompanying figure represents the form of regulator that has been used in all our distillations of large as well as small quantities of oils, together with the complete apparatus in the form for use. The regulator consists simply of a glass stopcock, *A*, better of considerable size, attached to the manometer by means of a side tube. To regulate closely the inflow of air an arm three to five feet in length, according to the working of the stopcock, is attached firmly to the head of

the cock, and supported in a manner easily movable within very small divisions on the arc of a circle of which it is the radius. To enable the operator to make adjustments while standing in front of the manometer, a piece of lead is attached as a weight to the upper end of the lever, and a cord is carried over a pulley, *B*, and terminates in a ring in front of transverse rows of pins a few millimeters apart. For economy of space the pulley is placed lower in the figure than its actual



position. The upper part of the lever consists of two strips of wood, with a space between, through which passes a rigid copper wire as a support and guide. When the lever is in a vertical position, the stopcock is fully open; any adjustment is easily obtained, and the manometer may be held stationary within one millimeter at any desired point during several hours.

In the distillation of small quantities of liquids, requiring constant attention, we have used a piece of glass tube 45–60 mm. long, attached to the side stopcock, with a sliding support near the end. In vacuum-distillations on a large scale it

is more convenient to refer to the entire length of the manometer column, since at any time leaks may occur that are indicated only on the lower portion of the graduated scale. With a short manometer column alone, much time may be lost in waiting for an exhaustion that is interfered with by leaks.

In heating the still, direct contact with the flame was prevented by maintaining an airspace above the burner by means of a sheet of asbestos. With such application of heat equally on the sides and bottom, there was less danger of decomposition at high temperatures. All but the highest distillates were collected in a Warren hot condenser containing a glass worm. With this condenser vacuum-distillations are easily controlled, and, as in distillations under atmospheric pressure, with a great economy of time. Continuous distillation is possible without losing the vacuum, by drawing in consecutive fractions through the rear tubulure of the retort. The two receivers shown in the figure are convenient, and some additional advantage would be gained by means of an independent vacuum connection with the lower receiver. Several supports are not represented in the figure. Much time and tedious labor were expended on this apparatus before all the difficulties were overcome; but the compensation was ample, since by means of it we have been able to separate in considerable quantities constituents of high boiling-points without decomposition, which otherwise would have been impossible. As an evidence of its usefulness, during several months continuous distillations were in progress, in charge of assistants, with highly satisfactory results. Distillates were collected at intervals of 10° , 5° , and 2° . The depression in boiling-points by the diminished pressure in vacuum-distillation varies between 60° and 65° for the lower constituents, and 125° or more for those collected between 300° and 350° . The residue above 350° (450 – 500° atmospheric pressure) in both Ohio and Canada oils had apparently undergone but little decomposition; in appearance, it was a thick, ready-flowing oil, with scarcely any odor.

A portion of the residual oil above 350° *in vacuo* was redistilled in an ordinary boiling-flask, and the temperatures of the

vapor and of the liquid were read on a Mahlke 550° thermometer. The oil began to distil with much decomposition at 385° in the vapor, and 415° in the liquid. One-half distilled with the temperature in the liquid below 430°. Doubtless the temperatures of distillation were much reduced by the decomposition. Since we have found that distillations below 250° may be carried on successfully without serious decomposition in an atmosphere of carbonic dioxide, when we return to the distillation of the higher constituents this method may be serviceable.

OHIO PETROLEUM.

In the study of Ohio petroleum I have been aided by Mr. E. J. Hudson.¹ Besides the publications from this laboratory on the sulphur compounds² and those of Orton,³ I am aware of no published statements concerning the composition of Ohio sulphur petroleum. The crude oil which formed the basis of our work was received from the Peerless Refining Company, Findlay, which controls a large section of oil territory. When received, it was of a somewhat thicker consistency than ordinary Pennsylvania oil, with a slight odor of hydric sulphide that is usually observed in crude sulphur oils. It contained a small quantity of water, which was removed completely only after long standing with fused calcic chloride. In determining the specific gravity of Ohio sulphur petroleum, oils were collected from wells at different points in the Findlay and Lima fields. The determinations were made at 20°.

Findlay Field.

	Specific gravity.
(1) Barnsville	0.8272
(2) Heilstone Oil Co., Well No. 2, Hancock County	0.8296
(3) Ohio Oil Co., Wood County	0.8194
(4) Langmade Well, No. 4, Portage, Hancock County	0.8149
(5) Peerless Refining Co., Well No. 2, Liberty, Hancock County	0.8278
(6) Peerless Refining Co., Well No. 5, Baltimore, Wood County	0.8239

¹ A part of this work formed the subject of a thesis by Mr. Hudson for the degree of Bachelor of Science.

² Proc. Am. Acad., 25, 218; this JOURNAL, 16, 83.

³ Ohio State Geological Reports, 1886, 1888, 1890; U. S. Geological Report, 1886-87.

Lima Field.

The following specimens of crude oil, representing different portions of the Lima and Findlay Fields, were received from the Ohio Oil Company, with a history of each well :

Township.	County.	Drilled.	Sand. Feet.	Oil. Feet.	Depth. Feet.	Production after shot. Daily.	Production at present. Daily.
(1) St. Mary's	Auglaize	May, 1872	1132	1147	1166	100 bbls.	5 bbls.
(2) Liberty	Hancock	Aug. 1893	1250	1273	1286	75 "	10 "
(3) Montgomery	Wood	Oct. 1892	1192	1197	1242	25 "	5 "
(4) Woodville	Sandusky	July 1892	1180	1195	1205	125 "	10 "
(5) Nottingham	Wells, Ind	April 1895	900	1004	1044	165 "	75 "
(6) Liberty	Wood	Sept. 1894	1152	1172	1227	125 "	30 "
(7) Lima	Allen						

Sp. gr.	(1)	(2)	(3)	(4)	(5)	(6)	(7)
	0.8288	0.8345	0.8265	0.8254	0.8243	0.8428	0.851

There is evidently an appreciable variation in the composition and properties of the oils from different points in the Ohio field. Marked differences occur in the specific gravity as well as in the percentages of carbon, hydrogen, nitrogen, and sulphur.

The oil that was employed in this examination was somewhat heavier, with a specific gravity 0.8380. These results show an appreciable variation even in different portions of the same field. A similar variation in specific gravity has been observed in other fields :

	Specific gravity.
Alsace (Pechelbronn), depth 146 feet (Engler)	0.906
" " " 213 "	0.885
Oelheim (Hanover)	0.889
Tegernsee	0.815
Pennsylvania	0.8185
"	0.801
Galicia	0.8235
Baku	0.859
"	0.810
Ohio (Mabery)	0.838
" (Markownikoff and Ogloblin)	0.887
Baku (Apscheron)	0.855-0.885
Galicia	0.835-0.895
American petroleum (Petrolitz)	0.830
" (Weil)	0.827
Canada (Markownikoff and Ogloblin)	0.828
"	0.844
Alsace (Pechelbronn)	0.668

The value 0.887 assigned by Markownikoff to Ohio oil is much higher than has elsewhere been given. It must have been obtained in an oil from another Ohio field, perhaps from the Mecca district. The values given by Markownikoff for Canada oil must refer to a product from the Oil Springs district, although the number 0.828 is lower than is usually found even in that oil. The numbers given by Redwood are 0.844–0.854 for Oil Springs oil, and 0.859–0.877 for Petrolia oil. In Oil Springs oil we found 0.8427–0.8389 (gas oil), 0.8442, and in Petrolia oil, 0.8553, 0.8621, 0.8800.

In ascertaining the quantity of sulphur by combustion in air in the crude oil from which distillates were prepared for examination, the following results were obtained: (1) 0.73 per cent., (2) 0.72 per cent., (3) 0.72 per cent. In oils previously examined the percentage of sulphur has not been above 0.60. Sulphur was also determined in the oils collected in the Findlay and Lima districts in the order of the numbers given above:

	Findlay.	Lima and Findlay.		Findlay.	Lima and Findlay.
(1)	0.33	0.61	(5)	0.68	0.56
(2)	0.63	0.71	(6)	0.61	0.76
(3)	0.56	0.37	(7)		0.81
(4)	0.68	0.49			

In Apscheron oil, Markownikoff and Ogloblin¹ obtained 0.064 per cent., and 0.16 per cent. in Trans-Caspian oil.

The percentages of carbon and hydrogen in the oil from which distillates were obtained were found by combustion in air with a layer of plumbic peroxide in front to retain the sulphur²: carbon, 84.57; hydrogen, 13.62. In other samples from Findlay and Lima carbon and hydrogen were also determined:

	C.	Findlay.	H.		C.	Lima and Findlay.	H.
(1)	85.76		13.56		84.73		13.48
(2)	85.82		13.80		84.03		13.05
(3)	84.33		13.46		83.89		13.18
(4)	84.35		13.36		84.55		13.55
(5)	84.20		13.41		83.41		13.13
(6)	84.18		14.60		85.07		13.33
(7)					85.00		13.05

¹ Ann. chim. phys. [6], 2, 393.

² Warren: Proc. Am. Acad., 6, 472.

The percentages of carbon and hydrogen that have been found in analyses of oils from other deposits are given in the following table :

	C.	H.	O.
Apscheron (Markownikoff and Ogloblin)	86.65	13.35	
“ “ “ “	87.01	13.22	
“ “ “ “	86.89	13.18	
Trans-Caspian “ “ “	86.75	12.19	
Egyptian (Kast and Kunkler) ¹	85.85	11.72	
Pechelbronn (Sainte-Claire Deville) ²	85.7	12.00	2.3
Galicja (St. Claire Deville) ²	82.2	12.10	5.7
Rangoon (St. Claire Deville) ²	83.8	12.7	3.5

The following values represent the percentages of carbon and hydrogen in crude petroleum from other American oil fields :

	C.	H.	O.
W. Virginia, Scioto Well (Peckham) ³	86.62	12.93	
W. Virginia, Cumberland Well (Peckman) ³		13.38	
California oil (Peckman) ³		11.82	
Mecca oil (Peckham) ³	86.32	13.07	
Canada, Manitoulin (Deville) ²	83.00	14.6	2.4
“ Petrolia “	84.5	13.5	2.0
“ West “	79.4	14.1	6.5
Ohio oil “	84.2	13.1	2.7
Pennsylvania oil “	83.4	14.7	1.9
“ “ “	84.19	13.7	1.4

In the crude oil used in this examination, and in the other specimens described above, nitrogen was determined by the Kjeldahl method, and several closely concordant results were obtained by combustion with soda-lime; the former gave 0.11 per cent., and the other oils the following percentages :

Findlay.	Lima and Findlay.
(1) 0.26 per cent.	0.068
(2) (a) 0.023, (b) 0.023 per cent.	0.047
(3) 0.21 per cent.	0.054
(4) 0.13 “	0.049
(5) 0.35 “	0.060
(6) 0.08 “	0.056
(7)	0.024

The presence of nitrogen in Ohio and Canadian petroleum

¹ Chem. Centrbl., 1890, p. 932.

² Compt. rend., 68, 485.

³ Geological Survey of California, 11, Appendix, p. 39.

will receive further attention at the close of this paper in some observations on the origin of petroleum.

The bromine absorption in the crude oils was determined by the method described in Allen's "Commercial Organic Analysis." A weighed quantity of the oil was allowed to stand in the dark with a slight excess of bromine dissolved in dry carbonic disulphide, and the portion not absorbed was titrated with standard solutions of sodic hyposulphite and iodine. The strength of the bromine solution was ascertained by parallel titrations. Approximately one per cent. of hydrobromic acid is evolved in these determinations in crude oils.

Findlay. Lima and Findlay.		Findlay. Lima and Findlay.			
(1)	11.29	8.74	(5)	13.07	10.93
(2)	14.62	9.31	(6)	11.32	12.31
(3)	10.55	11.49	(7)		12.06
(4)	14.89	12.30			

A comparison of the bromine-absorption of the sulphur oils with that of oils from other sources indicates that bromine-absorption is independent of sulphur compounds, and a distinctive property of petroleums in general. The following determinations were made :

Chinese petroleum	10.90 per cent.
Italian petroleum	7.10 "
Macksburg, O., petroleum	9.74 "
Berea Grit, O., petroleum	10.71 "
California petroleum	9.88 "

The quantities of bromine absorbed by distillates from the crude sulphur oil were also determined :

Fractions.	Percentage of bromine absorbed.
110-150°	0.73
150-220°	1.74
220-257°	4.84
257-300°	5.04
300-330°	12.10
Residue	19.50

Throughout this investigation some reliance has been placed on the absorptive capacity for bromine of crude oils and distillates obtained from them as indicating a certain unsaturated condition. While it should be borne in mind that a considerable proportion of the bromine-absorption is due to

the sulphur constituents, there is besides a large absorption in the crude oils and in the residues of distillation above 350° by other constituents. There is much yet to be learned concerning the decompositions in distillations at high temperatures, which are indicated by the greatly increased bromine-absorption, and the study of the higher-boiling portions will be greatly facilitated by the aid of the Mahlke thermometers for observing temperatures below 550° .

The characteristic qualities of Ohio oil appear also in the proportions that distil at different temperatures; 800 grams of the crude oil collected in the following proportions beginning at 110° :

	110-150°.	150-220°.	220-257°.	257-300°.	300-350°.	Residue.
Grams	76	133	86	76	69	348
Percentage	9.75	16.63	10.75	9.75	8.63	43.5
Sp. gr. at 20°	0.7282	0.7669	0.7940	0.8138	0.8242	0.8976
Percent. sulphur	0.10	0.38	0.41	0.36	0.37	0.54

The distillates below 235° were colorless, and no odors resulting from decomposition were observed. Above this point color appeared in the distillates, with the odor of decomposition, which became more marked with increasing temperatures. Above 275° the heavier paraffin-oils began to distil. In refinery-distillation of Ohio petroleum it is therefore evident that cracking begins in the vicinity of 250° . No doubt crude sulphur petroleums undergo decomposition spontaneously to some extent, since upon standing they always contain hydric sulphide. We find that certain unstable constituents separated from the crude oils gradually become darker in color, with other indications of chemical change. At the beginning of the distillation hydric sulphide came off in considerable quantities, but after the first fraction very little appeared in the succeeding distillates below the point where decomposition began.

On account of the viscous character of the Ohio and Canadian petroleums and the large proportion of heavy oils, temperatures indicated by the thermometer in the vapor of the distillates should be higher than the corresponding temperatures of the oil. To ascertain this difference, crude Findlay oil was distilled, and the temperature of the distillates and of the oil were noted with the following results:

Thermometer in the oil.	Thermometer in the vapor.	Difference.
167°	120°	47°
180°	140°	40°
203°	160°	43°
221°	180°	41°
238°	200°	38°
259°	220°	39°
282°	240°	42°
301°	260°	41°
318°	280°	38°
341°	300°	41°

Except in the first reading the average difference in temperature is about 40°.

Determinations of sulphur in the crude oil and in the distillates obtained from it, showed that considerable sulphur was lost during distillation. In order to obtain definite information concerning the quantity lost, 100 grams of the crude oil were distilled under atmospheric pressure, and attached to the receiver were flasks containing a solution of sodic hydrate for the purpose of absorbing any hydric sulphide that escaped. In front of the flask containing hydric sulphide there was connected another flask, which contained alcohol, with a delivery tube in front to absorb volatile products that might result from decomposition. The oil was fractionated to 300°, collecting between 115° and 250°, and between 250° and 300°, and the hydric sulphide was determined after oxidation with bromine by precipitation with baric chloride. The percentage of sulphur in the several fractions was also determined. As usual in distillation of the sulphur petroleums, a slight sublimate of sulphur was observed in the neck of the condenser. Upon diluting the alcohol it became slightly turbid, which indicated probably some volatilization of sulphur constituents. The alkaline solution of the sulphur from the distillate 115-250° gave 0.1135 gram of baric sulphate, corresponding to 0.0156 gram of sulphur. From the alkaline solution of the sulphur absorbed from the fraction 250-300°, 0.6946 gram of baric sulphate was obtained, corresponding to 0.0958 gram of sulphur. A determination of sulphur in the distillate 115-250° gave 0.55 per cent.; in the distillate 250-300°, 0.51 per cent.; and in the residue above 300°,

0.60 per cent. Since the weight of the distillate collected at 115–250° was 20.55 grams, the weight at 250–300°, 5.1 grams, and the weight of the residue above 300°, 74.35 grams, the total weight of sulphur accounted for in these determinations was 0.7166 gram, leaving 0.27 gram which must have escaped in ways not determined.

In comparing the quantities of the distillates from Ohio oil, and their specific gravities, with those obtained by Markownikoff and Ogloblin¹ in the Apscheron oil with a specific gravity at 17° of 0.882, and those given by Bolley from Pennsylvania petroleum with a specific gravity of 0.816, it is evident that the properties of Ohio petroleum place it between the Caucasus and Pennsylvania oils.

The Caucasus oil began to distil at 120° in the vapor, and 180° in the liquid.

APSCHERON.			PENNSYLVANIA.			OHIO.		
Parts in 100. Sp. Gr.			Parts in 100. Sp. Gr.			Parts in 100. Sp. Gr.		
120–150°	0.5	0.786	19.70			110–150°	9.75	0.7282
150–200°	10.9	0.824	8.84	0.757		150–220°	16.63	0.7669
200–250°	12.8	0.861	15.23	0.788		220–257°	10.75	0.7940
250–320°	24.7		20.7	0.809		257–300°	9.75	0.8138
						300–350°	8.63	0.8242
<hr/>			<hr/>			<hr/>		
Total	48.9		64.48			55.51		
Residue	52.1		35.52			43.00		

While the temperatures at which the Ohio oil was collected are slightly different from the others, they are sufficiently close for comparison.

Kramer² has compared the quantities of distillates obtained from crude petroleum of other fields:

	Sp. Gr.	–150°	150–250°	250–300°	Residue
Tegernsee	0.812	20.04	26.12	14.00	35.91
Pennsylvania	0.814	14.34	25.35	13.75	40.99
Baku	0.880	0.63	12.73	15.55	37.95
Oelheim	0.885	0.74	11.05	9.75	75.71
Alsace	0.888	1.3	16.37	17.07	47.88

Taubes Barlâdu³ distilled 1115 cc. of crude Roumanian petroleum from the deposits on the south slope of the Car-

¹ Ber. d. chem. Ges., 16, 1873. ² Chem. Centrbl., 1887, p. 290.

³ Ztschr. ang. Chem., 1889, p. 606.

pathians, which are probably connected with the Galician oil zone, with the following results:

	cc.	Per cent. by volume.
30-125°	150	13.5
125-225°	385	35.5
225-280°	160	14.3
280-315°	98	8.1

In an examination of Burmese petroleum, Romanis¹ obtained an oil from Yay-nan-Chaung with a specific gravity of 0.8590, which solidified at 24°. An oil from Arracan with a specific gravity of 0.825 at 32° contained considerable benzol and other aromatic hydrocarbons. Upon distillation, the following results were obtained:

	Per cent.	Distilled with steam.	
70-90°	3.1	°	Per cent.
90-100°	7.6	—100°	23.3
100-130°	10.6	100-110°	33.0
130-200°	18.7	110-130°	29.3
200-300°	18.7	Residue	13.3 (heavy oil)
+300°	12.5		98.9
Oil in residue	8.0		
Paraffin	3.1		
Loss	17.7		
	<hr/> 100.00		

Markownikoff and Ogloblin examined the ash of Caucasus petroleum by igniting the residue of distillation. They found 0.09 per cent. of ash calculated for the original quantity of crude oil, and it consisted chiefly of the oxides of calcium, iron, and aluminum. Traces of copper and silver were also found. We have determined by combustion in oxygen the percentages of carbon and hydrogen in coke from the refinery residue of the distillation of Ohio petroleum; the percentage of carbon was 95.06, and that of hydrogen 4.85. A determination of nitrogen by the Kjeldahl method gave 0.31 per cent. The quantity of ash in the coke was determined by burning off the carbon, and the weight of ash thus obtained corresponded to 0.11 per cent. of the coke burned. In attempting to estimate the percentage of ash in the crude oil from the amount found in the coke, there is some uncertainty as to

¹ Chem. News, 59, 292.

the quantity of oil corresponding to the coke. In some oils the proportion of residue is estimated at ten per cent. of the crude oil. It depends also upon the method followed by the refiner. Sometimes the first distillation of the crude oil is pushed to the point of complete decomposition, and the tar distillate is again distilled until it is coked. It is well known that earthy matter frequently remains for some time in suspension in the crude oil after it is taken from the wells. On this account, if the oil were distilled before the suspended material had subsided, the ash would not represent what had been in solution in the oil. But the oil is usually allowed to stand some time before distillation, and that the coke we examined was practically free from suspended matter is evident from the low percentage of ash, and corresponding results with Canadian oil where the ash was determined in a tar distillate and in coke from crude oil; the percentages of ash from the two sources were not very different.¹

In Findlay oil, in which our determination was made, the proportion of still-residue is doubtless somewhat smaller than that mentioned above, probably between ten and five per cent. The corresponding percentage of ash in the crude oil would, therefore, be not far from 0.005, an amount considerably less than Markownikoff and Ogloblin found in Russian oil.

An analysis of the ash showed that it was composed chiefly of lime and magnesia, and the quantity of magnesia is at least equal to that of the lime. Traces of iron and aluminum were found, the iron possibly having been dissolved from the still. It is therefore evident that the crude oil has exerted an appreciable solvent action on the limestone reservoir, dissolving both constituents of the dolomitic rock.

It is maintained by some chemists that all petroleums contain the same series of compounds in different proportions, and that the difference in properties depends upon a variation in the quantities of the constituents. In a general sense, with respect to the principal series of hydrocarbons, this is doubtless true; yet there is such a wide difference in the properties of oils like those from Pennsylvania and the Caucasus that they are characteristic of substances quite unlike. The

¹ *Vide* Determination of Ash in Canadian Petroleum; second part of this paper.

Caucasus petroleum is wholly, or nearly, wanting in the series $C_n H_{2n+2}$, and the Pennsylvania oil evidently contains the series $C_n H_{2n}$ in much smaller proportion than the Russian oil. The presence of the higher members of the latter series in the Pennsylvania oil has yet to be ascertained. It is conceivable that the difference in the composition of petroleums is due to the different influences to which they have been exposed. Perhaps greater porosity of the reservoir or cover where oils exist under pressure has permitted an escape from certain oils of the more volatile constituents, especially of the series $C_n H_{2n+2}$. If this should be demonstrated by more extended observations, it would be reasonable to expect the same bodies in the Pennsylvania as in the Russian oil, only in smaller quantities of the higher constituents. Referring the sulphur in Ohio petroleums to the average composition of the compounds containing it, the crude oil should contain at least 5 per cent. of the sulphur derivatives. Evidently such a large proportion of the sulphur compounds in petroleum must exert an important influence on its properties, and we should therefore expect a marked difference between the sulphur petroleums and those which contain only traces of sulphur.

From a general similarity of Ohio petroleum to the oil from Pennsylvania, so far as it relates to hydrocarbons of the series $C_n H_{2n+2}$, it should perhaps be expected that the composition of the latter oil, which has been established beyond question, at least so far as the portions of low boiling-points are concerned, should represent also similar portions of the Ohio products. As mentioned above, even a casual examination of the sulphur oils affords abundant evidence that their peculiar properties depend upon other constituents than the hydrocarbons $C_n H_{2n+2}$. While these unique constituents may detract from, rather than enhance, the value of the sulphur oils for commercial purposes, it is as important for the intelligent guidance of the refiner as it is interesting from a scientific point of view that they be well understood.

While occupied with the sulphur compounds in Ohio petroleum, I was impressed with the complexity in composition manifested by the products of distillation, and with the importance of a thorough examination for all constituents. We

therefore began with an endeavor to separate and identify the individual homologues of methane which have been found in Pennsylvania petroleum, including an approximate quantitative determination of all but the more volatile members.

HYDROCARBONS C_nH_{2n+2} .

To separate the hydrocarbons of lower boiling-points we obtained 25 liters of the very first distillate from a 300-barrel still. This distillate contained 0.10 per cent. of sulphur. Considerable gas always escapes in refinery-distillation before a liquid distillate appears, but we have not yet undertaken an examination of its composition. Probably this is essentially the same as that of the gas given off in beginning a distillation of Pennsylvania oil together with hydric sulphide, which is always evolved to a greater or less extent in the distillation of sulphur petroleums. Sadtler¹ found that the gas from Pennsylvania wells consisted principally of methane, with some ethane, nitrogen, and hydrogen. In the gas from Canada wells, at Enniskillen, Fouqu  ² found marsh gas, ethane, and small quantities of carbonic dioxide. According to Ronalds,³ the gas from Pennsylvania petroleum contains 1.27 per cent. of carbonic dioxide, 6.58 per cent. of oxygen, 54.00 per cent. of nitrogen, and 38.15 per cent. of ethane and propane; by exposing the escaping gas to a freezing-mixture, butane was condensed to a liquid.

In an exhaustive study of natural gas from Pennsylvania wells, Phillips⁴ found that the principal constituents were hydrocarbons C_nH_{2n+2} , with nitrogen in variable proportions and carbonic dioxide in small quantity, but no hydrogen nor carbonic oxide.

The crude distillate was subjected to fractional distillation in a porcelain still, to which was attached a Warren condenser filled with a mixture of salt and ice, with ice alone, or with water, according to the fractions collected. Another ordinary condensing-worm surrounded with a freezing-mixture was placed in front. Subsequent distillations were conducted in glass stills, and the fractions rapidly accumulated within limits of temperature which distinguish the hydrocarbons C_nH_{2n+2} .

¹ Am. Chemist, 1876, p. 97.

² Compt. Rend., 67, 1045.

³ J. Chem. Soc., 18, 54.

⁴ This JOURNAL, 16, 406.

At the beginning of the first and second distillations, a delivery-tube was attached to the bottle receiving the distillate, and extended so as to collect in a receiver inverted over water any volatile constituents that might have escaped condensation. At first a very little gas collected, which burned with a smoky flame, but none afterwards. The following quantities were collected during the first distillation :

	-25°	25-30°	30-35°	35-40°
Grams	525	400	450	400

After the fourth distillation 35 grams collected between 0° and 1°, distilling for the most part at 0°, barometer 740 mm. This was evidently butane, boiling-point 0°. Inasmuch as the boiling-point of this hydrocarbon has been carefully determined,¹ further examination was not deemed necessary. The temperature rose rapidly to 5°, and, between 7° and 9°, 20 grams of a distillate collected, mostly between 7° and 8°, the boiling-point of a hydrocarbon which was separated by Warren from Pennsylvania petroleum, and which was regarded by him as one of the butanes. Since the atmospheric temperature was in the vicinity of 30° when these distillations were in progress, special care was necessary to preserve the distillates, and the ice accidentally becoming exhausted in the ice-chest, the distillate collected at 0° burst the bottle, and the one at 8° forced out the stopper and volatilized. Of the two possible butanes, the boiling-point of one is without question 0°. The other seems to have been obtained by Butlerow² from isobutyl alcohol, and the boiling-point assigned to it was -17°.5. Under more favorable conditions, we shall collect a larger quantity of this distillate, to determine by its chemical behavior, as well as by its constancy in boiling-point, whether it be a definite compound.³

¹ Ronalds : J. Chem. Soc., **18**, 54 ; C. M. Warren : Mem. Amer. Acad. (N. S.), **9**, 156.

² Ann. Chem. (Liebig), **144**, 10.

³ We have since obtained 50 grams of an oil that collected at 8-9° with very small amounts above and below these limits. A vapor-density determination by the Hofmann method gave the following results :

0.0717 grams of the oil gave 45.5 cc. of vapor at 16°, and under a tension of 48.1 cm. of mercury.

Required for C₄H₁₀.

2.01

Found.

2.04

For further proof as to the composition of this distillate, an examination of its halogen and other derivatives is now in progress.

Considerable quantities of distillates collected below 30° , but by continued distillation they were mostly separated into higher and lower constituents, indicating the absence of individual products. In the vicinity of 30° the fractions were large, amounting to 300 grams between 28° and 32° . After the ninth distillation, 75 grams collected between 29° and 30° , with the barometer at 747 mm. A vapor-density determination gave 2.52; required for pentane, 2.49. This product was, therefore, isopentane, boiling-point 30° . Between 36° and 37° , 75 grams distilled, and this distillate was shown by its vapor-density to have the composition required for pentane; a vapor-density determination gave 2.49; required for pentane 2.49. This substance therefore corresponded to normal pentane, boiling-point 37° (Warren). The weights collected evidently afforded no information concerning the proportions in which these hydrocarbons are contained in the crude oil. Other results show that they are present in smaller quantities than in Pennsylvania oil.

At higher temperatures to 60° , the weights of the distillates were very small and irregular, which indicates the absence of definite compounds. Between 60° and 62° , 150 grams collected at the end of the fifteenth distillation, and this was still further reduced to 50 grams between 60° and 61° , with a vapor-density corresponding to that of hexane; found, 2.94; required for hexane, 2.98; boiling-point of isohexane, $61^{\circ}.27$ (Warren). After the fourteenth distillation, with the barometer at 749 mm., between 67° and 68° , 75 grams collected that distilled tolerably constant within this limit. A vapor-density determination gave 3.00; required for normal hexane, 2.98; boiling-point, $68^{\circ}.5$ (Warren).

For the separation of the less volatile hydrocarbons, the fraction -150° , obtained from the crude oil by distillation *in vacuo*, was subjected to further distillation under atmospheric pressure. 41.5 kilos of crude Findlay oil were distilled under a tension of 50 mm., and collected in the first distillation at -100° , $100-150^{\circ}$, $150-200^{\circ}$, $200-250^{\circ}$, and $250-350^{\circ}$. The decomposition was comparatively slight, and the fractions, especially the less volatile, were free from the disagreeable pungent odors characteristic of refinery-distillates. Even the

residue above 350° had apparently undergone very little decomposition. On account of the reduced boiling-points, it was not expected that the more volatile constituents could be collected, and it was subsequently found that scarcely any distillate boiling below 30° was condensed. The weights of the first fractions were as follows:

	-100°	$100-150^{\circ}$	$150-200^{\circ}$	$200-250^{\circ}$	$250-350^{\circ}$	Residue
Grams	8000	8520	6480	7700	2670	9000
Percentages	18.6	19.8	15.1	18.0	6.2	20.9

The specific gravity of the individual fractions was determined with the following results:

-100°	$100-150^{\circ}$	$150-200^{\circ}$	$200-250^{\circ}$	$250-300^{\circ}$	$300-350^{\circ}$	Residue.
0.7445	0.7852	0.8161	0.8387	0.8647	0.8759	0.0130

The fraction -100° contained no hydric sulphide; the higher fractions contained it in small quantities. The percentages of sulphur in the same distillates were obtained by combustion in air:

	-100°	$100-150^{\circ}$	$150-200^{\circ}$	$200-250^{\circ}$	Residue.
Sulphur	0.054	0.25	0.42	0.61	0.67

In comparing the percentages of sulphur in the vacuum-distillates with those under atmospheric pressure, it is evident that the main bodies of the sulphur compounds collect in the higher portions, leaving the fractions below 150° nearly free from sulphur.

Percentages of sulphur under atmospheric pressure:

$110-150^{\circ}$	$150-220^{\circ}$	$220-257^{\circ}$	$257-300^{\circ}$	$300-350^{\circ}$	Residue.
0.10	0.38	0.41	0.37	0.37	0.54

It is also apparent that distillation *in vacuo* protects, to a certain extent, the sulphur compounds from decomposition. In ordinary distillation of the crude oil, as has been mentioned, sulphur is invariably observed in the condensing-tube. Even in vacuum-distillation at high temperatures decomposition cannot be wholly avoided, although the separation of sulphur has never been observed. It is probable that chemical reactions occur within the oil from the action of the various constituents upon one another, such, for example, as the action of the oxygen compounds upon the sulphur compounds. These observations furnish valuable evidence in favor of vacuum-distillation for the sulphur petroleums.

The percentage of bromine absorbed by the fractions collected *in vacuo* was also determined :

	-100°	100-150°	150-200°	200-350°	Residue.	Crude oil
Bromine	0.0	4.57	6.60	7.08	24.38	10.19

It is interesting to compare the bromine-absorption in the vacuum-distillates with the quantities absorbed in the distillates collected under atmospheric pressure :

	100-159°	150-220°	220-257°	257-300°	300-330°	+330°
Bromine	0.73	1.74	4.84	5.04	12.10	19.50

Doubtless the larger absorption of bromine in the vacuum-distillates at lower temperatures depends, at least in part, upon the fact that the sulphur compounds are protected from decomposition during distillation, and also upon the extent to which the constituents with higher boiling-points are distilled at lower temperatures under the diminished pressure. It would be expected that the residue in the distillation under atmospheric pressure should show a higher absorptive power than that collected *in vacuo*. The behavior of the higher fractions towards bromine and the nature of the decompositions by cracking will receive further attention.

The portions distilling below 150° were next submitted to prolonged fractional separations under atmospheric pressure with the aid of Hempel columns and Warren condensers. We were led to appreciate the exhaustive labors of our predecessors in their investigations on petroleum, and our indebtedness to them for the efficient means at present available for conducting such distillations. For the separation of complex mixtures, especially in considerable quantities, in point of efficiency the Warren condenser leaves nothing to be desired. It appears to effect a more rapid separation than the Hempel column, although the latter is of great service. The Hempel method has the advantage that it requires less attention, with no loss of time in heating a bath nor in maintaining a constant temperature in the bath. From the description of Warren's hot condenser given in the "Treatise on Chemistry," Vol. III, Part I, by Roscoe and Schorlemmer, an erroneous impression must have been received concerning this apparatus. On pp. 149, 150, the following words appear: An apparatus has been employed by Warren in the fractional

distillation of tar oils and petroleums. This permits a complete control over the temperature of the vapor, accomplished by an air-bath round which a spiral tube is placed, connected with the boiling-flask. The temperature of this air-bath is regulated by a lamp. The liquid used for heating the air-bath may be either water, oil, or fusible metal, and into this the thermometer is placed. . . . In distilling petroleum the difference in temperature between the boiling liquid and the air-bath was, to begin with, about 35° , or even more." The idea conveyed here is that the constant temperature is maintained by means of an air-bath, although it is evident from the following description, taken from the original memoir,¹ that there is not the remotest allusion to an air-bath: "In the new process, perfect control of the temperature of the vapors is secured by simply conducting these vapors upwards through a worm contained in a bath, the temperature of which is regulated by means of a lamp, or by a safety furnace. The bath may be of oil or water or metal for very high temperatures, as the case may require, and it is furnished with a thermometer. That this bath may be equally adapted for the separation of liquids boiling below the common temperature, an empty vessel is permanently secured in the interior of the bath by means of straps of metal across the top, to serve as a convenient receptacle for ice or ice-water, by means of which a low temperature may be steadily maintained. This interior vessel also serves a good purpose in economizing time and fuel in heating the bath, and it diminishes the quantity of oil required to cover the worm. It is made to extend to within about three inches of the bottom of the bath, and large enough to fill a greater part of the space in the center of the coil." It will therefore be seen that it was not Warren's intention to use this apparatus in any sense as an air-bath. It is to be used solely as a liquid-bath.

Since the principal object was to identify the individual constituents and to determine their approximate quantities, it was only necessary to collect our products within such close limits of temperature comparable with boiling-points already accurately determined that they should yield satisfactory

¹ Mem. Amer. Acad. (N. S.), 9, 125.

analytical data. In successive distillations, collecting at first within 5° , then within 2° , and finally within 1° , after the first distillation the fractions collected rapidly, with increasing quantities at temperatures near boiling-points of well-known hydrocarbons C_nH_{2n+2} , and at certain other points at which an equilibrium in boiling-points seemed to be established by mixtures. It was only with much difficulty that some of these mixtures could be separated into their constituents. We had occasion to recall the remark of Warren concerning the greater amount of labor involved in determining the absence of definite compounds in such mixtures than in proving the presence of well defined hydrocarbons. The fractions containing the aromatic hydrocarbons will be considered together. The products collected for vapor-density determinations were purified as completely as possible by the removal of unsaturated hydrocarbons, sulphur compounds, and the aromatic hydrocarbons. For the removal of sulphur compounds, each fraction was thoroughly agitated with alcoholic mercuric chloride. After washing with water there remained in solution not more than 0.02 or 0.03 per cent. of sulphur when the mercuric chloride gave a crystalline precipitate, which was the case in distillates below 150° , provided they were collected at first *in vacuo*. In a former paper¹ it was stated that alcoholic mercuric chloride removed two-thirds of the sulphur. Those experiments were made with refinery distillates, which do not behave the same towards mercuric chloride as vacuum-distillates. In higher fractions somewhat more sulphur is retained, and with increasing boiling-points even the mercury itself in considerable quantity may be held in clear solution, either in the form of $HgCl_2R_2S$, or in some other combination. This peculiarity has occasioned us much trouble in purifying distillates above 200° . In some of these products, hydric sulphide in the cold will not precipitate the mercury; frequently it is only after prolonged action with the aid of heat that the mercury can be completely removed. These sulphur oils seem to possess the property of dissolving metals, metallic oxides, and other compounds, which has been observed in other petroleum. The action of paraffin

¹ This JOURNAL, 16, 88.

oils on metals has been examined by Macadam,¹ who finds that lead, solder, and zinc are quite readily, tin and iron but slightly, affected. Some oils have a greater solvent action than others, and Macadam attributes it to the hydrocarbons. Engler² repeated the experiments of Macadam, and observed that metals were not affected when air is excluded. It was therefore inferred that acid compounds are formed in the oil by exposure to air, and also metallic oxides, which are dissolved by the acids. Engler does not attribute the solvent action to ozone. It is probable that the purification of refinery-distillates from the sulphur petroleums, by agitation with an alkaline solution of plumbic oxide, depends, at least in part, upon the solvent action of certain constituents of the oil. Oxygen compounds, which are doubtless present in these oils, may assist the action, as has been observed in other oils. This subject will receive further attention when we reach the higher distillates.

After removal of the sulphur compounds, each distillate for vapor-density determination was thoroughly agitated, first with concentrated nitric, then with concentrated sulphuric acid, washed, and dried. Finally, under a return condenser, it was heated for some time with metallic sodium.

From 41.5 kilos, distilled *in vacuo*, at the end of the eighth distillation, the last seven under atmospheric pressure, the following weights were obtained with much smaller quantities outside these limits :

	-55°	58-62°.	65-68°.	77-83°.
Grams	15	120	310	85

As already mentioned, on account of loss from the diminished pressure, as well as the unavoidable loss in any distillation, the weights of the lower fractions collected *in vacuo* evidently cannot be accepted as representing even approximately the quantities present in the crude oil.

Between 87° and 93°, 80 grams collected after the sixth distillation, and in the portion which distilled constant at 89-90°, bar. 754 mm., a vapor-density determination gave 3.43; required for isoheptane, 3.46; boiling-point 90°.4 (Warren).

At the end of the sixth distillation, 175 grams collected at

¹ J. Chem. Soc., 1878, p. 355.

² Ber. d. chem. Ges., 11, 2186.

96–99°, and 50 grams distilled constant at 86–97°, bar. 744 mm.; a vapor-density determination of this product gave 3.42; required for heptane, 3.6; boiling-point of heptane, 98.7° (Warren). Above this point the distillates were small in amount to 109°, where other products began to appear; between this point and 120° the single degree fractions were considerable in quantity.

At 118–120°, 120 grams were collected, of which 50 grams distilled constant at 119–120°, bar. 749 mm. This product gave a value in a determination of its vapor-density required for octane: found, 3.98; required, 3.94. Since some doubt has been expressed concerning the existence of an octane with this boiling-point, this fraction was carefully purified for analysis, with alcoholic mercuric chloride, nitric acid, and sulphuric acid, and it was finally submitted to prolonged boiling with sodium. Determinations of carbon and hydrogen then gave the following results:

I. 0.1707 gram oil gave 0.5282 gram CO_2 and 0.1707 gram H_2O .

II. 0.2017 gram oil gave 0.6237 gram CO_2 and 0.2737 gram H_2O .

	Calculated for C_8H_{18} .	I.	Found.	II.
C	84.20	84.42		84.28
H	15.79	15.19		15.08

The low percentage of hydrogen evidently indicated that the octane was still contaminated by a hydrocarbon containing less hydrogen. For further purification the oil was heated to boiling during several hours with a mixture of nitric and sulphuric acids, and boiled several times with sodium. It then gave the percentages of carbon and hydrogen required for octane:

	Required for C_8H_{18} .	Found.
C	84.20	84.20
H	15.79	16.10

There seems to be no question that the fraction 118–119° contains a hydrocarbon with the composition required for octane, and this observation is apparently confirmed by the results of others. Warren¹ separated a constituent of Pennsyl-

¹ Proc. Am. Acad., 27, 78.

vania petroleum distilling constant at $119^{\circ}.5$ (cor.), which gave a vapor-density corresponding to that of octane. From the extraordinary care with which the determinations of Warren were made, there can be no doubt as to the existence of a hydrocarbon with this boiling-point in Pennsylvania petroleum. Although hexahydroisoxylol has been recognized by Beilstein and Kurbatoff,¹ it is probably not the principal constituent with this boiling-point of the Pennsylvania oil; it is certainly not of the Ohio oil.

From coal-oil, Schorlemmer² separated an octane boiling at $119-120^{\circ}$, and subsequently he identified the same body in petroleum boiling at 119° . The following data are taken from his original publication:

	Required for C_8H_{18} .	Found. ¹
C	84.20	84.10
H	15.79	16.10
Vapor-density	3.98	3.95

In the "Treatise on Chemistry," by Roscoe and Schorlemmer, (New York, 1886), it is stated that the three octanes known are normal octane, boiling-point $125^{\circ}.46$, found in petroleum; tetramethylbutane, boiling at $108^{\circ}.5$; and hexamethylethane, melting at $96-97^{\circ}$ and boiling at $105-106^{\circ}$. This enumeration does not recognize an octane boiling at 119° in petroleum. It would seem that our fraction from the Ohio oil was prepared with sufficient care to preclude the possibility of a mixture of higher or lower constituents. We shall endeavor to obtain independent evidence as to the identity of this fraction by a study of its chemical reactions, and the preparation of its derivatives.

The following suggestions, which I have taken from one of the private papers, dated 1868, of Mr. Warren, through the kindness of Professor Storer, indicates that Warren recognized the possibility of a series containing less hydrogen: "The samples analyzed may have contained traces of more highly carbonized substances, and that it would be worth while to treat with $HOSO_2$ and $HONO_2$, and remove these." Beilstein and Kurbatoff met with the same difficulty in the fraction $95-100^{\circ}$ and $118-120^{\circ}$ in their attempts to ascertain the

² Ber. d. chem. Ges., **13**, 1208.

¹ J. Chem. Soc., **15**, 419.

presence in the Pennsylvania oil of the hexahydro series. The series with less hydrogen seems to be removed only very slowly even by vigorous treatment with a mixture of nitric and sulphuric acids.

In continuing the separations above 120° , after the eleventh distillation the oils collected in considerable quantities within the limits of one degree :

	120-121°	121-122°	122-123°	123-124°	124-125°	125-126°	126-127°	127-128°
Grams	35	40	80	70	75	75	60	40

Notwithstanding our endeavors to separate the fractions $122-125^{\circ}$ into higher and lower constituents, they may still be mixtures; aromatic derivatives are here present in small quantity. If in more prolonged separations distillates still persist within the same limits, they will be submitted to careful study in their behavior toward chemical reagents.

The greater portion of the fraction $125-130^{\circ}$ was unfortunately lost by an accident after the eleventh distillation. Sufficient however was collected at $127-128^{\circ}$ for a vapor-density determination; it gave, by the method of Dumas, the value required for the formula C_8H_{18} ; found 3.90, required 3.94. To the liquid collected by Warren at this point was assigned the boiling-point $127^{\circ}.6$; the vapor-density found by him was 3.99, and those observations seem to be confirmed by our results with the Ohio product. The portions distilling between 115° and 130° evidently need to be carefully examined in larger quantities with particular reference to the octanes. The distillates collected between 130° and 145° will be considered in connection with the aromatic compounds.

Between 144° and 148° , after many distillations, the fractions were small in quantity. At the end of the sixth distillation, 65 grams collected at $149-151^{\circ}$, of which 40 grams distilled constant at $149-150^{\circ}$, barometer 756 mm. After prolonged heating with concentrated nitric acid a nitro compound was formed that remained chiefly in solution in the oil. Upon dilution of the acid an oily liquid separated in small quantities. But when the oil was shaken with sodic hydrate, it became intensely red in color, and by repeated washing with the alkaline solution the nitro product was in part removed, and it separated again as an oil by acidifying the solution. After

washing, the remaining oil was dried and heated to boiling during several hours with sodium. It was then distilled from the large quantity of solid that had separated, and the greenish yellow distillate again boiled with sodium. Still more solid separated, and after distillation the oil was again treated with sodium until there was no further action. The boiling-point was not appreciably changed by this treatment, although it was evident that some constituent had been removed capable of forming a nitro derivative soluble in alkalis. The residual oil was shown by vapor-density determinations and analysis to have the composition required for nonane. The boiling-point of nonane is $150^{\circ}.8$ (Warren).

I. 0.1799 gram oil gave 0.3987 gram CO_2 , and 0.1749 gram H_2O .

II. 0.1751 gram oil gave 0.5424 gram CO_2 , and 0.2488 gram H_2O .

	Calculated for C_9H_{20} .	I.	Found. II.
C	84.37	84.96	84.48
H	15.63	15.16	15.88

Analysis I. was made of the oil after treatment with alcoholic mercuric chloride, but before heating with the acid mixture; analysis II. of the oil after treating with a mixture of nitric and sulphuric acids and boiling with sodium.

The determinations of vapor-density of this product in the apparatus of Victor Meyer, with a bath of ethyl benzoate, gave the following results: I. 4.73; II. 4.74; required for C_9H_{20} , 4.43.

This fraction therefore contains nonane, although it consists to a very considerable extent of another hydrocarbon, which seems, by the ready formation of nitro compounds and its behavior toward alkaline solvents, to be a member of the series C_nH_{2n} . All the fractions of the Ohio oil that we have examined below 150° are similarly contaminated by, or rather contain in appreciable quantities, hydrocarbons which form nitro products with the characteristic qualities of an unsaturated or paraffin nitro compounds.

Thus far Ohio petroleum has proved to contain members of the series $\text{C}_n\text{H}_{2n+2}$, corresponding to those which have been

identified in Pennsylvania oil, but in much smaller quantities. They form one-fifth of the crude Pennsylvania oil and less than one-tenth of Ohio oil.

In identifying these constituents it has not seemed necessary to accumulate data further than would appear essential in showing the similarity of our products to those whose composition has been so carefully demonstrated in Pennsylvania petroleum. And while this portion of our labor may be of less interest than the study of the constituents with higher boiling-points, it has seemed of sufficient importance to justify the necessary expenditure of time and effort. The higher fractions have been quite thoroughly distilled entirely *in vacuo* to avoid decomposition so far as possible, and these products, as well as the residue above 350° of the first vacuum-distillate, are reserved for later study.

(To be continued.)

ON THE COMBINATION OF ANHYDROUS AMMONIA AND ALUMINIUM CHLORIDE.

BY J. M. STILLMAN AND MINNIE B. YODER.

The compounds resulting from the action of dry ammonia upon anhydrous metallic salts, especially the halogen salts, have been more or less carefully studied by chemists, notably by H. Rose and by Rammelsberg, though many others have contributed to the interesting data. Inspection of the results of these investigations shows that no very satisfactory relation can be perceived between the composition of these compounds and the natural-group relationships of the elements from which they are derived. It appeared to be of interest to study some of these compounds more carefully to see if such relationship might not be found to exist, and if, from this as a starting point, some clue might not be obtained to the chemical nature of such compounds. The replaceability of water by ammonia in hydrated copper sulphate noted by Mendelejeff¹ lends additional interest to the study of these compounds. Like the combined water in salts the ammonia in these addition-products furnishes a good illustration of a kind of chemical union, but little understood and frequently characterized

¹ Ber. d. chem. Ges., 3, 422.

as "Molecular Combination." As conflicting data exist concerning the composition of the combinations of ammonia and ferric chloride, the action of ammonia upon ferric and ferrous chlorides was first studied, the investigation being carried on by Mr. A. S. Miller.¹ The result of this investigation was to show that ferric chloride combines with dry ammonia to form $\text{FeCl}_3 \cdot 6\text{NH}_3$, a light, reddish, non-deliquescent powder, which loses ammonia to the air, leaving $\text{FeCl}_3 \cdot 5\text{NH}_3$ as a compound relatively more stable in dry air. At higher temperatures it loses ammonia with gradual oxidation and formation of ammonium chloride. The action of ammonia upon ferrous chloride was found to conform to earlier data, yielding a white powder $\text{FeCl}_2 \cdot 6\text{NH}_3$, losing 4NH_3 at 100° in dry hydrogen.

The general similarity of aluminium and ferric compounds suggested that the ammonia compounds of aluminium chloride be next studied.

The data on this subject are comprised in the investigations of Persoz² and H. Rose.³ The former obtained a compound containing as high as 27.6 per cent. ammonia; the latter one containing 25.7 per cent., thus suggesting $\text{AlCl}_3 \cdot 3\text{NH}_3$ (or $\text{Al}_2\text{Cl}_6 \cdot 6\text{NH}_3$) as the formula (theory, 27.7 per cent). The re-investigation of this combination was taken up much on the same lines as were laid down for the study of the iron compounds. The aluminium chloride was obtained by heating aluminium foil in a current of carefully dried chlorine gas. The chloride was purified by sublimation in the same tube and current of chlorine in which it was prepared. It possessed a yellow color and gave a faint test for iron, but was practically pure.

Al found	20.46
Al in AlCl_3 (calculated)	20.52

The treatment with ammonia gas was at times undertaken in a U bent in the combustion-tube, in which the chloride was prepared, or else the chloride was transferred with especial care to avoid access of atmospheric moisture to an ordinary U-tube. To avoid so far as possible secondary reactions resulting from the heat of reaction on absorption of ammonia,

¹ This JOURNAL, 17, 570.

² Ann. chim. phy. [?], 44, 320; cited by Graham-Otto, 5th Auf. IV, 2, 31.

³ Cited by Graham-Otto: *loc. cit.*

the U-tube was immersed in water and carefully dried ammonia was passed through, at first very slowly and mixed with much air. Only when the granular yellowish chloride had fallen into a fine white powder was ammonia passed through so as to replace the air in the apparatus to effect complete saturation. The entire time thus employed for saturation was usually about twenty hours. The resulting product is a white and very light powder, occupying many times the volume of the original chloride.

It is not deliquescent, and when thrown into water is not dissolved, but passes over naturally into hydrate of aluminium. It smells strongly of ammonia.

The following analyses were made each from an independent preparation :

	I.	II.	III.	IV.	Calculated for $\text{AlCl}_3.6\text{NH}_3$.
Al	11.47	11.49	11.47	11.66	11.47
Cl	44.53	44.64	44.73	44.89	45.22
NH_3	39.92	40.96	41.51	41.40 41.94	43.31
	<hr/> 95.92	<hr/> 97.09	<hr/> 97.71	<hr/> 97.95 98.49	<hr/> 100.00

It will be seen that the ammonia falls noticeably short and that the total percentages are short of 100. We shall have occasion to speak of this later, but in general it will be seen that the analyses point unmistakably to the formula $\text{AlCl}_3.6\text{NH}_3$ as expressing the composition of the saturated product.

In view of the results of Persoz and of Rose above quoted, attempts were made to ascertain the stability of this compound at various temperatures in perfectly dry air, by passing a slow current of dried air through U-tubes containing the saturated product.¹ The U-tube was reimmersed in a water or paraffin-bath and the temperature regulated as desired. The results obtained were not what we had anticipated. While the determination of aluminium and chlorine in samples treated at tem-

¹ Great care was taken to dry all the gases thoroughly; chlorine was passed through concentrated sulphuric acid and glacial phosphoric acid; ammonia was generated by dropping ammonia-water on stick potash, and dried through two cylinders of stick potash and two of quick-lime; air was passed through sulphuric acid and through cylinders of stick potash and phosphoric acid. Appropriate drying tubes were also connected beyond the U-tubes to prevent the entrance of moisture from that direction.

peratures from 20° to 120° were approximately such as to indicate a composition $\text{AlCl}_3 \cdot 5\text{NH}_3$, the ammonia determinations fell considerably short of the percentage theoretically present.

The following examples will illustrate:

Time treated by current of dry air.	Tempera- ture.	Per cent. Al.	Per cent. Cl.	NH ₃ .
48 hours	20-25°	11.69	45.25	31.77
72 "	20-25°	12.57	48.19	33.03
9 "	100°			
24 "	100°	12.37	47.03	23.23
120 "	20-25°	12.07	48.04	undet.
5 "	100°			
4 "	120°	12.21	49.01	?
100 "	20-25°	12.23	46.82	21.80
13 "	110°			
Calculated for $\text{AlCl}_3 \cdot 5\text{NH}_3$		12.36	48.74	38.90

When we first met with these results we feared that the loss of ammonia had been more or less compensated by absorption of moisture, but increased precautions to obviate this contingency made this explanation improbable. We were then forced to conclude that a more radical decomposition takes place. We also noticed that in two instances drops of moisture collected on the cooler parts of the tube when the current of air had been interrupted for a time, and the temperature of the U-tube was above 100°. We could not account for this except on the assumption that the water was produced by the oxidation of the hydrogen of the ammonia.

To test this tendency to oxidation, dry air was passed over a portion of the saturated ammonia compound heated to about 200° for a period aggregating twenty-four hours. A noticeable deposition of moisture took place when the air current was interrupted. Ammonium chloride was produced and collected by volatilization in the cooler parts of the tube as a well characterized crystalline sublimate.

The analysis of the substance remaining in the U-tube gave

Al	28.10
Cl	31.11
NH ₃	15.87
	<hr/>
	75.08

If we here assume that all the aluminium has been oxidized

to the oxide Al_2O_3 , and that all the chlorine is present as ammonium chloride—ignoring for the moment the determination of ammonia above given—we should have for 28.10 per cent. aluminium, 24.96 per cent. oxygen, and for 31.11 per cent. chlorine we should have 15.82 per cent. ammonium. The 15.87 per cent. ammonia above found would correspond to 16.81 per cent. ammonium. The analyses would then be expressed:

Al	28.10
O	24.96
Cl	31.11
NH_4	15.82
	<hr/>
	99.99

These results taken in connection with the observed formation of water and the isolation of some ammonium chloride by sublimation render the result of the oxidation process quite plain.

We also are disposed to connect the shortage in ammonia and in totals of analyses in the original preparation with this oxidation. In spite of the cooling of the U-tubes during absorption, it is probable that the very considerable energy of the chemical action produces local increase of temperature and consequent oxidation of the aluminium and of the ammonia. If instead of using air to dilute the ammonia we had used nitrogen or hydrogen, it is probable that results still more close to the theory would have been obtained.

A couple of experiments were made to determine the stability of the preparations at higher temperatures in a current of hydrogen.

A portion of the saturated compound (analyzed under III) was heated for ten hours at 200–240° in a current of dry hydrogen. The semi-fused and somewhat hygroscopic mass gave the following results on analysis:

		Calculated for $\text{AlCl}_3 \cdot 2\text{NH}_3$.
Al	16.12	16.1
Cl ¹	59.45	63.6
NH_3	19.76	20.3
	<hr/>	<hr/>
	95.33	100.00

¹ Not enough of the preparation remained to duplicate this analysis as seemed desirable.

A portion of the saturated compound (analysis under IV.) was submitted to a current of dry hydrogen for twelve hours at room-temperature to replace air thoroughly and then heated in a free current of hydrogen for six hours at 100° .

The analysis gave :

		Calculated for $\text{AlCl}_3 \cdot 5\text{NH}_3$.
Al	12.03	12.36
Cl	47.56	48.74
NH_3	35.03	38.90
	<hr/>	<hr/>
	94.62	100.00

As the original preparations were slightly oxidized, no very satisfactory analyses were to be expected from these preparations. While the hydrogen was thoroughly dried it was not purified from possible contamination with other impurities. Nor is any stress placed here upon the definiteness of these compounds, nor their stability at the temperatures given, but a general idea of the stability of the combination at various temperatures may be obtained from the above results.

It did not seem advisable at present to repeat the investigation out of contact with oxygen for the sake of obtaining more exact analyses. It is intended to pursue in this laboratory the investigation of the action of dry ammonia upon other anhydrous chlorides, and it is not improbable that side-lights will be shed upon some of the questions raised in the foregoing from the behavior of other compounds.

Special emphasis is here laid upon the evident similarity of the results of the action of ammonia upon the chlorides of iron and aluminium.

THE CHEMICAL KINETICS OF OXIDATION.

BY HERMAN SCHLUNDT AND ROBERT B. WARDER.

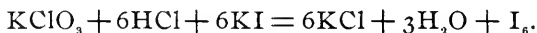
I.—ON THE SPEED OF THE LIBERATION OF IODINE IN MIXED SOLUTIONS OF POTASSIUM CHLORATE, POTASSIUM IODIDE, AND HYDROCHLORIC ACID.¹

BY HERMAN SCHLUNDT.

A systematic study of the conditions of experimentation that determine the progress of a reaction has until of late years received very little attention. During the last two decades the speed of various reactions as dependent upon modifying influences has been specially investigated, and to-day the subject of chemical dynamics furnishes many interesting problems for investigation. The present work has been undertaken with the view of collecting data for the solving of some of these problems.

Burchard² studied the speed of the liberation of iodine in mixtures of hydriodic and iodic acids in very dilute solutions. Similarly he investigated mixtures of hydriodic acid with bromic or chloric acids. Mixtures of the salts of hydriodic and chloric acids with hydrochloric acid, however, have never to my knowledge been investigated in this way. It is the purpose of this paper to study the speed of the liberation of iodine in such mixtures as are influenced: first, by temperature; second, by degree of concentration; third, by the presence of an excess of one or more of the components; and fourth, by the addition of an excess of other acids.

Preliminary Experiments.—It is well known that when potassium iodide, potassium chlorate, and hydrochloric acid are mixed in solution, iodine is liberated according to this reaction.



In order to ascertain the conditions favorable for studying the speed of the liberation of iodine in such mixtures, several preliminary experiments on the effects of temperature and concentration became necessary. It was found that in mix-

¹ This paper is an abstract of a thesis submitted for the degree of Bachelor of Science in the General Science Course, University of Wisconsin, June, 1894, and issued as a Bulletin of the University in the same year.

² Ztschr. phys. Chem., 2, 796, (1888).

tures containing equivalents¹ of the salts according to the foregoing reaction as decinormal solutions at 0° iodine is liberated very slowly, a sample of 20 cc. of the mixture after twenty-four hours requiring only 0.1 cc. of a decinormal solution of sodium thiosulphate to destroy the blue color produced by the addition of starch-paste. The same mixture at 100° proved well adapted for investigation, as the following table shows :

Duration of reaction in minutes.	Cc. of solution taken.	Cc. of n-20 $\text{Na}_2\text{S}_2\text{O}_3$ used in each titration.	Per centage of iodine liberated.
15	20	1.45	3.6
35	20	3.1	7.8
60	20	4.3	10.8
90	20	6.0	15.0

Preparation of Solutions.—The solutions used were prepared as follows : A normal solution of potassium iodide free from iodate served throughout the investigation. It was prepared by dissolving 165.54 grams of the pulverized salt, dried at 100°, and making it up to one liter. The normal hydrochloric acid was standardized on calcite. The potassium chlorate was tested for sulphates, nitrates, chlorides, the heavy metals, and the alkaline earths, and found to be pure. The solution of this salt was three times normal and was prepared by taking 61.25 grams of the dry crystallized salt to a liter. A twentieth-normal solution of sodium thiosulphate served for titration. It was prepared by dissolving 12.4 grams of the pure crystallized salt per liter of water. The strength of this solution was verified by testing with decinormal iodine solution. The starch-paste used was quite dilute and was prepared by stirring up 2-3 grams of the fine starch with cold water ; 300-400 cc. of boiling hot water were then added and the mixture well stirred. This paste was then filtered, and the filtrate used as indicator. A fresh solution was frequently prepared.

Conduct of Experiments.—The entire series of investigations was conducted at 100°. The mixtures were prepared by measuring out the desired equivalents of the different components, cooling them to 0° in ice-water, and then mixing

¹ Whenever this term is used it is understood to mean equivalents according to the reaction already given.

them. Samples of 20 cc. of the mixture were then quickly taken out and put into ordinary six-inch test-tubes. The tubes were quickly sealed, but all the time kept as cool as possible. The samples were then plunged into a large kettle of boiling water and kept at this temperature. At definite intervals samples were taken out and plunged into ice-water, thus quickly checking the reaction. After one minute the test-tubes were broken, washed with cold water, and the iodine determined by means of a twentieth-normal solution of sodium thiosulphate.

The test-tubes were sealed at about the same distance from the end, thus keeping the pressure nearly constant. Whenever it was found expedient to work with samples of 10 cc. the tubes were used over again. As the test-tubes were new, special precautions in cleaning had to be exercised. To remove the alkalis that are given off by new glassware, I followed the advice of Professor Ostwald and steamed the tubes for about five minutes by means of an apparatus figured on p. 295 of his "*Hand- und Hilfsbuch zur Ausführung physico-chemischer Messungen.*"

In mixtures where the components enter in equivalent proportions it was found that the free iodine began to crystallize out when about 40 per cent. had been liberated. To get this iodine into solution a few cc. of a strong potassium iodide solution were added. But as this excess of potassium iodide might possibly enter into the reaction and so slightly increase the amount of sodium thiosulphate used, the iodine of several samples was shaken out with carbon bisulphide and determined. A comparison of results obtained by these two methods,¹ shows that the addition of a few cc. of cold potassium iodide during titration has little or no effect on the result.

The equation expressing the reaction shows that for every molecule of potassium iodide present one atom of iodine is liberated. In titrating the iodine with sodium thiosulphate the following reaction takes place :



Hence the per cent. of iodine liberated at any time from the given sample (originally containing 20 cc. of potassium

¹ Sec. B, III, series (1) and (3), and Sec. C, series (4).

iodide in decinormal solution) is obtained by dividing by 40 the number of cc. of sodium thiosulphate used, the thiosulphate being twentieth-normal.

Presentation of Results.—The results obtained are divided into 5 sections. Section A includes the results obtained from a mixture containing equivalents of the salts as decinormal solutions. The effect of a definite excess of *one* of the several components upon the speed of the reaction is shown in Section B. Section C, similar to B, gives the effect upon the speed when definite excesses of *both* potassium iodide and hydrochloric acid are used. Section D gives the results obtained from mixtures containing equivalents of the components in fifth-normal and two-fifths-normal solutions respectively. The acceleration in the speed by various organic and inorganic acids forms the fifth and last section of the results.

To facilitate comparison, the results obtained in similar series are graphically represented in the same figure. In plotting the curves the axis of abscissas was chosen to denote the time of the reaction, each space representing one hundred minutes, while the percentages of iodine liberated are plotted on the axis of ordinates.

The results are given in condensed form in the following tables.

Table I shows the progress of the reaction :

A, with equivalent decinormal amounts, according to the reaction: $\text{KClO}_3 + 6\text{HCl} + 6\text{KI} = 7\text{KCl} + 3\text{H}_2\text{O} + \text{I}_6$; B, with two-fold quantity of chlorate at the beginning; C, with three-fold quantity; and D, with four-fold quantity of chlorate at the beginning.

A sample of 400 cc. of the mixture A was prepared as follows :

Normal hydrochloric acid	40.0 cc.
Normal potassium iodide	40.0
Three-times normal potassium chlorate	13.3
Water	306.7
	<hr/>
	400.0

20 cc. of the mixed solution were taken for each titration:

TABLE I.

Time in minutes.	Cc. n-20 $\text{Na}_2\text{S}_2\text{O}_3$ used in each titration. ¹				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
10		1.35		2.8		3.4		7.0
15	1.45		2.8	5.0	3.6		7.0	
20		2.85				7.1		12.5
30		{ 3.95 3.9	5.0	5.0		{ 9.9 9.8 }	12.5	
35	{ 3.1 3.0				{ 7.8 7.5 }			
40				8.25				20.6
55			8.0				20.0	
60	4.3	{ 6.6 6.7		10.6	10.8	{ 16.5 16.8 }		26.5
70	4.6				11.5			
85			10.95	13.5			27.4	33.8
90	6.0				15.0			
100		9.9				24.8		
110	6.6			15.4	16.5			38.5
120			12.7				31.8	
150	7.85		14.25	17.35	19.6	35.6		43.4
170		13.0				32.5		
180				19.25				48.1
210	9.4		16.65	20.25	23.5		41.6	50.6
230				21.4				53.5
270		16.9				42.3		
290				21.85				54.6
300	{ 12.05 12.25				{ 30.1 30.6			
360	13.55				33.9			
400			21.45				53.6	
420		18.95				47.4		
440	14.55			24.2	36.4			60.5
510				24.75				61.9
520	15.55				38.9			
585	16.0				40.0			
590		21.2	23.9	25.6		53.0	59.8	64.0
730	17.0				42.5			
830	18.4			27.4	46.0			68.5
900				27.8				69.5
1250	21.3				53.3			
1320		28.85	28.95	31.3		64.6	72.4	78.3
1400	22.7				54.3			
1830	23.2				58.0			
2000	24.1				60.3			

¹ See curves A, B, C, and D in Figure 1.

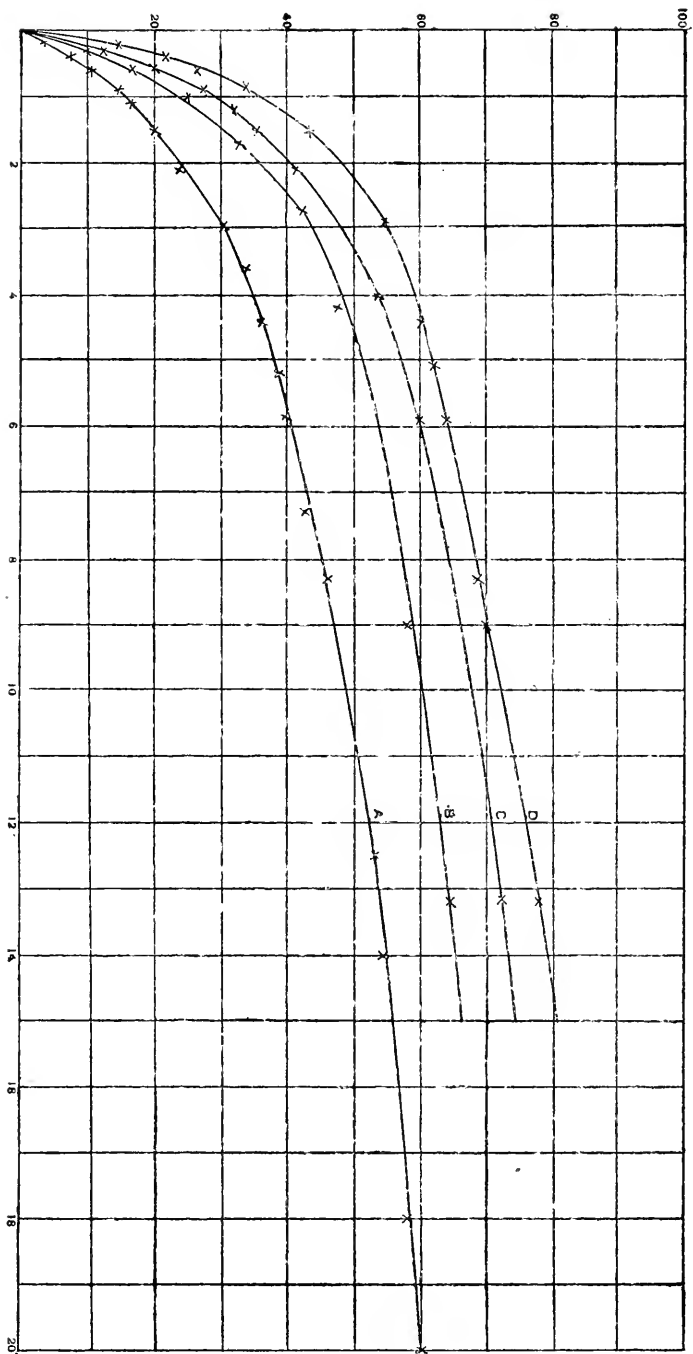


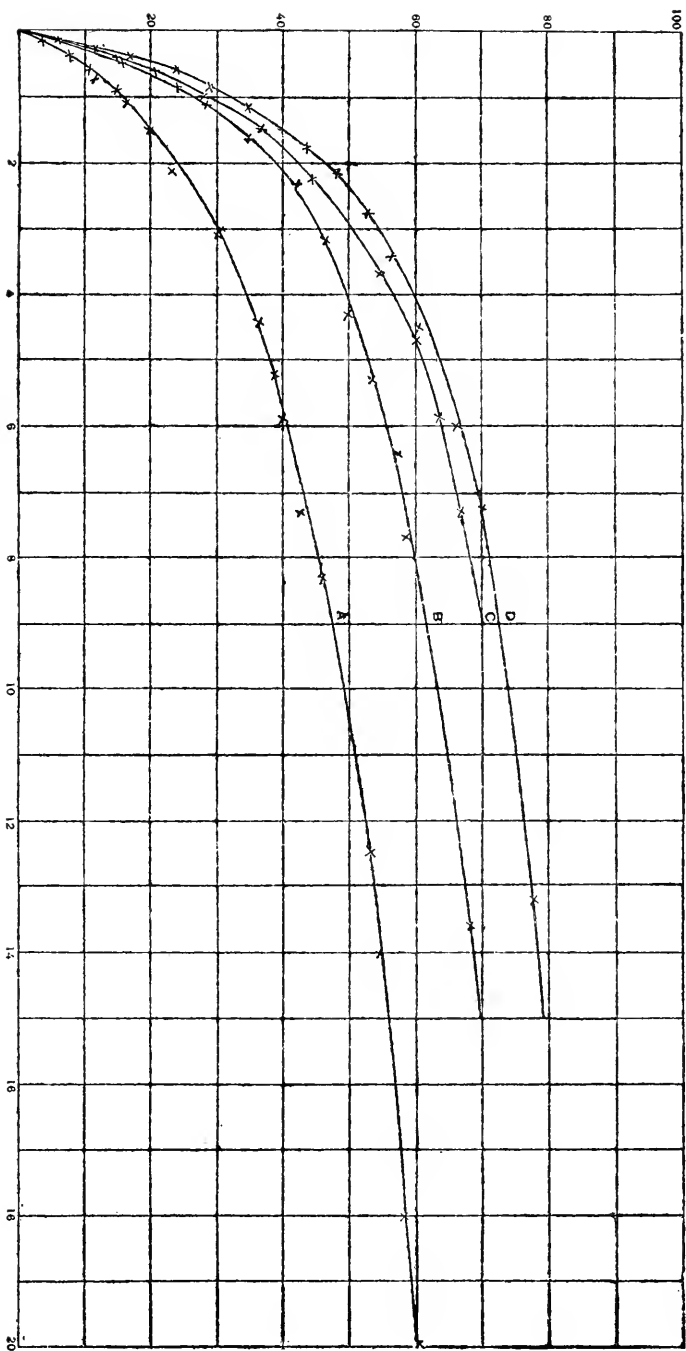
Table II shows the progress of the reaction :

A, with equivalent decinormal solutions; B, with two-fold quantity of potassium iodide, at the beginning; C, with three-fold quantity; and D, with four-fold quantity.

TABLE II.

Time in minutes.	Cc. n-20 $N_2S_2O_3$ used in each titration. ¹				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
10			1.8	1.9			4.5	4.8
15	1.45	2.4			3.6	6.0		
20			3.25				8.1	
25				4.6				11.5
30		4.7				11.8		
35	{ 3.1 3.0				{ 7.8 7.5			
40			5.9	6.7			14.8	16.8
50		6.35				15.9		
60	4.3			9.5	10.8			23.8
65			8.25				20.6	
70	4.6				11.5			
85		9.65		11.5		24.1		28.8
90	6.0				15.0			
100			11.05				27.6	
110	6.6	11.45			16.5	28.6		
115				13.75				34.4
150	7.85		14.6	17.1	19.6		36.5	42.8
160		13.85				34.6		
175				17.4				43.5
210	9.4				23.5			45.8
215				18.3				
225			17.8				44.5	
230		16.7				41.8		
275				21.15				52.9
300	{ 12.05 12.25				{ 30.1 30.6			
315		18.55				46.4		
340				22.6				56.5
360	13.55				33.9			
370			21.7				54.3	
430		19.9				49.8		
440	14.55				36.4			
450				24.2				60.5
470			24.0				60.0	
520	15.55				38.9			
530		21.4				53.5		
585	16.0		25.35		40.0		63.4	

¹ See corresponding curves, Fig. II.



Time in minutes.	Cc. n-20 $\text{N}_2\text{S}_2\text{O}_3$ used in each titration. ¹				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
600				26.3				65.8
640		22.9				57.3		
720			26.65	28.0			66.6	70.0
730	17.0				42.5			
760		23.65				59.1		
830	18.4				46.0			
1250	21.3				53.3			
1320				31.0				77.5
1360		27.2				68.0		
1400	21.7				54.3			
1830	23.2				58.0			
2000	24.1				60.3			

Table III shows the progress of the reaction :

A, with equivalent decinormal amounts ; B, with two-fold quantity ; C, with three-fold quantity ; D, with four-fold quantity of hydrochloric acid at the beginning.

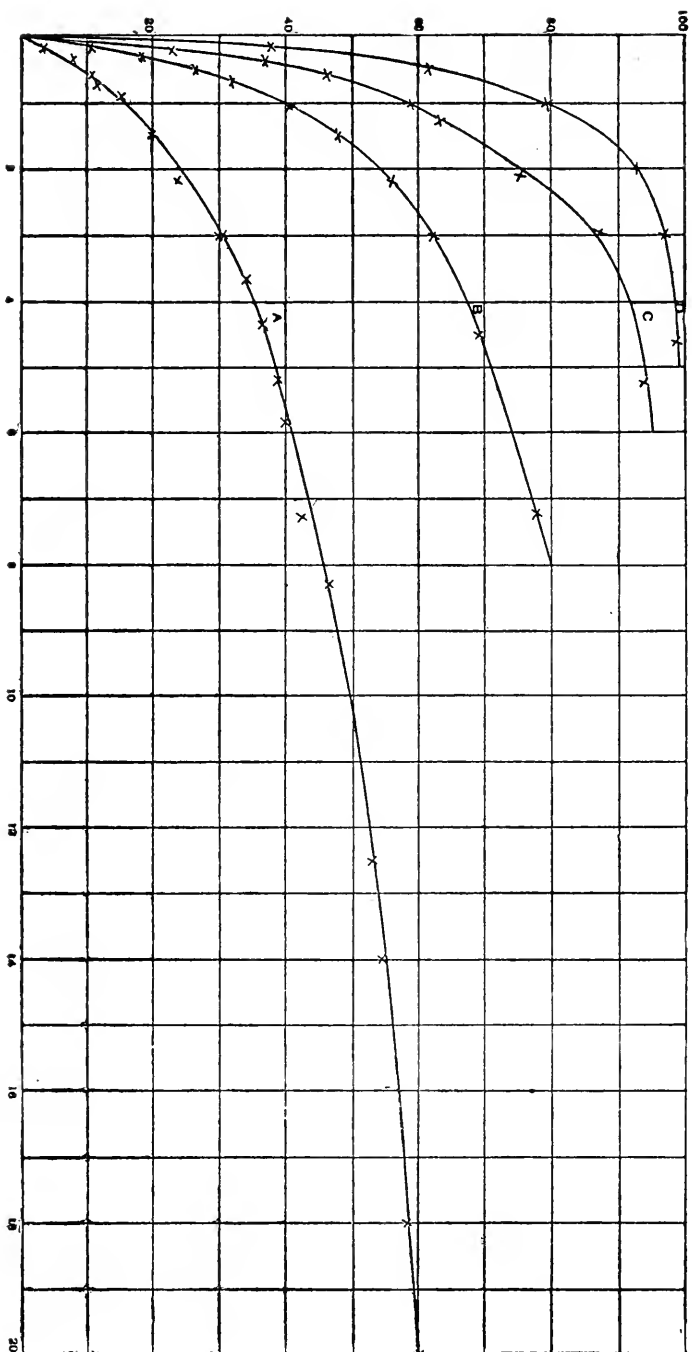
TABLE III.

Time in minutes.	Cc. n-20 $\text{Na}_2\text{S}_2\text{O}_3$ used in each titration. ²				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
10			4.6				11.5	
15	1.45				3.6			
17		4.3				10.8		
20			9.05	15.3			22.6	38.3
30		7.25				18.1		
35	{ 3.1 3.0				{ 7.8 7.5			
40			14.75				36.9	
50		10.45		24.55		26.1		61.4
60	4.3		18.75		10.8		46.4	
70	4.6	12.7			11.5	31.8		
90	6.0				15.0			
100			23.6	{ 31.7 ³ 81.8			59.0	{ 79.3 79.5 }
105		{ 16.35 ² 16.2				{ 40.0 40.5		
110	6.6				16.5			
130			25.35				63.4	
150	7.85	18.95			19.6	47.4		
200				37.15				92.9
210	9.4		30.1		23.5		75.3	
220		22.3				57.5		
295			34.95				87.4	

¹ See corresponding curves, Fig. II.

² See corresponding curves, Fig. III.

³ Iodine shaken out with carbon bisulphide.



Time in minutes.	Cc. n-20 $\text{Na}_2\text{S}_2\text{O}_3$ used in each titration. ¹				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
300	12.05	24.85		38.85	30.1	62.1		97.1
	12.25				30.6			
360	13.55				33.9			
440	14.55				36.4			
450		27.55				68.9		
460								
520	15.55			39.55	38.9			98.9
525			37.5				93.8	
585	16.0				40.0			
720		30.95				77.4		
730	17.0				42.5			
830	18.4				46.0			
1250	21.3				53.3			
1400	21.7				54.3			
1830	23.2				58.0			
2000	24.1				60.3			

¹See corresponding curves, Fig. III.

IV.

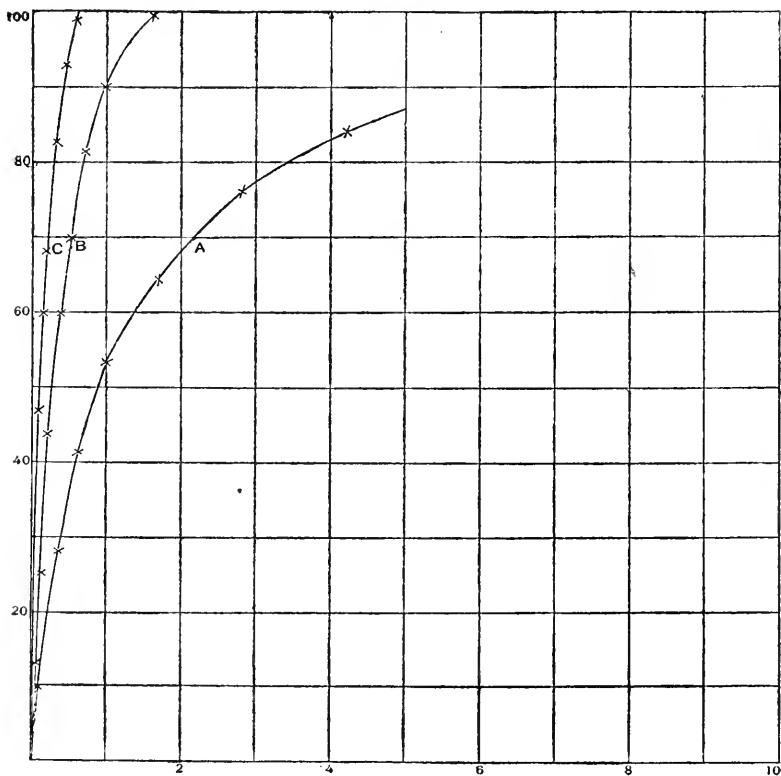


Table IV shows the progress of the reaction :

A, with two-fold quantities ; B, with three-fold quantities ; C, with three-fold quantities of hydrochloric acid and potassium iodide at the beginning ; D, with two-fold quantity of potassium iodide and six-fold quantity of hydrochloric acid at the beginning.

In series B, C, and D 10 cc. of the mixed solution were taken for each titration.

TABLE IV.

Time in minutes.	Cc. n-20 $\text{Na}_2\text{S}_2\text{O}_3$ used in each titration. ¹				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
5		2.6	5.4	7.3 ²		13.0	27.0	36.5
10	3.75	5.05	9.4	11.6	9.4	25.3	47.0	58.0
15			12.0				60.0	
20		8.75	13.7	{ 15.4 ² 15.45		43.8	68.5	{ 77.0 77.3 }
25			25.3				76.5	
30			16.5				82.5	
31				17.65				
35	11.35	12.0	17.3	18.1 ²	28.4	60.0	86.5	88.5
45			18.6	19.0			93.0	90.5
50		14.15				70.8		95.0
55			19.75				98.8	
60	16.5		19.95	19.9 ²	41.3		99.8	
70		16.25				81.3		99.5
80			19.9				99.5	
85				19.9				
95		17.85				89.3		99.5
100	21.3				53.3			
105			20.1				100.5	
160		19.8				99.0		
170	25.75				64.4			
280	30.4				76.0			
415	33.6				84.0			

Table V shows the progress of the reaction :

A, with equivalent decinormal amounts ; B, with equivalent fifth-normal amounts ; C, with equivalent two-fifths normal amounts.

In series B and C 10 cc. of the mixed solution were taken for each titration ; in series A, 20 cc. were taken for each test.

¹See corresponding curves, Fig. IV.

²Iodine shaken out with carbon bisulphide.

V.

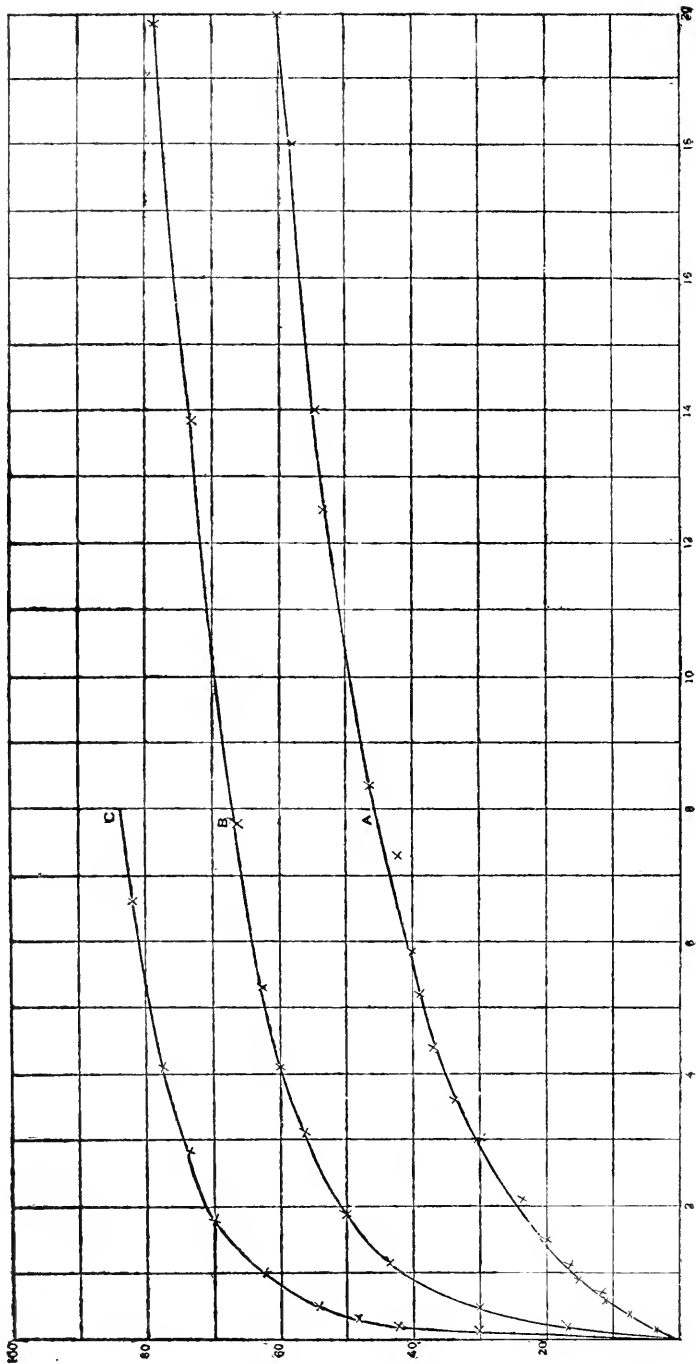


TABLE V.

Time in minutes.	Cc. n-20 $\text{Na}_2\text{S}_2\text{O}_3$ used in each titration. ¹			Percentage of iodine liberated.		
	A.	B.	C.	A.	B.	C.
10		4.45	24.25		11.1	30.3
15	1.45			3.6		
20		6.7	33.7		16.8	42.1
30			38.4			48.0
35	{ 3.1 3.0 }			{ 7.8 7.5 }		
50		11.95	43.3		29.9	54.1
60	4.3			10.8		
70	4.6			11.5		
90	6.0			15.0		
100			50.55			63.2
110	6.6			16.5		
115		17.3			43.3	
150	7.85			17.35		
180			55.6			69.5
190		20.1			50.3	
210	9.4			23.5		
280			58.7			73.4
300	{ 12.05. 12.25 }			{ 30.1 30.6 }		
310		22.5			56.3	
360	13.55			33.9		
410		23.9	61.75		59.8	77.2
440	14.55			36.4		
520	15.55			38.9		
530		25.15			62.9	
585	16.0			40.0		
660			65.0			81.25
750	17.0			42.5		
780		26.65			66.6	
830	18.4			46.0		
1250	21.3			53.3		
1380		29.2			73.0	
1400	21.7			54.3		
1830	23.2			58.0		
1980		30.4			76.0	
2000	24.1			60.3		

Table VI shows the progress of the reaction in fifth-normal solutions :

A, with no excess of acid at the beginning ; B, C, D, and E, with a definite excess of sulphuric acid, nitric acid, hydro-

¹ See corresponding curves, Fig. V.

chloric acid, and hydrobromic acid, respectively, at the beginning.

The following is a general sample mixture of 200 cc. :

Normal hydrochloric acid	40.0 cc.
Normal potassium iodide	40.0
Three-times normal potassium chlorate	13.3
Normal acid used as accelerator	20.0
Water	86.7
	<hr/>
	200.0

10 cc. of the mixed solution were taken for each titration.

TABLE VI.

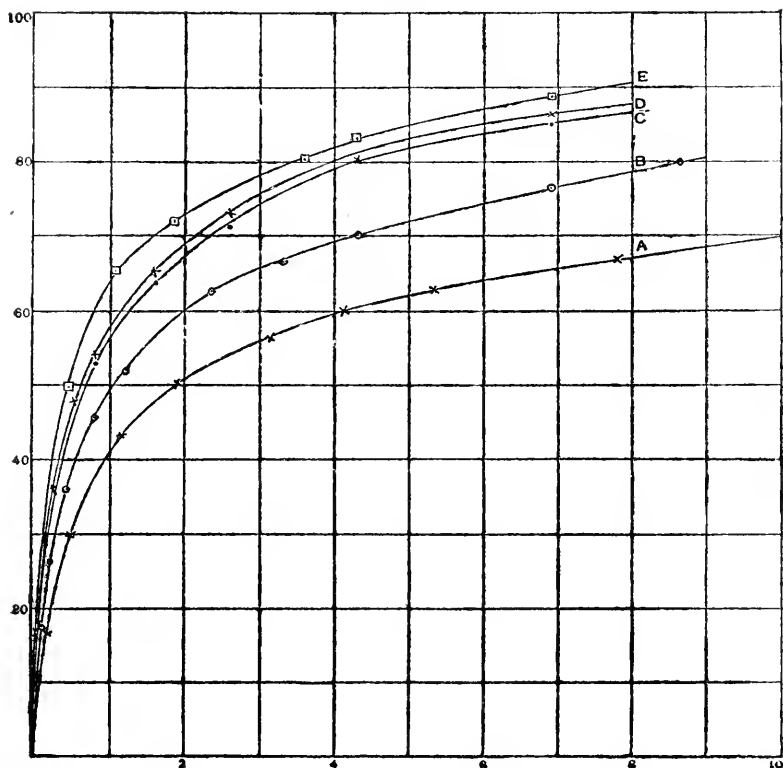
Time in minutes.	Cc. n-20 $\text{Na}_2\text{S}_2\text{O}_3$ used in each titration.					Percentage of iodine liberated.				
	A.	B.	C.	D.	E.	A.	B.	C.	D.	E.
10	4.45	6.1	7.2	7.2	8.0	11.1	15.3	18.0	18.0	20.0
20	6.7		11.4	11.5	12.6	16.8		28.5	28.8	31.5
25		10.55					26.4			
30			14.1	14.4				35.3	36.0	
45		14.4					36.0			
50	11.95				19.6	29.9				49.0
55			18.6	19.1				46.5	47.8	
80		18.25		21.6			45.6		54.0	
110			21.15		26.1			52.9		65.3
115	17.3					43.3				
120		20.8					52.0			
160				26.1					65.3	
185			25.45		28.9			63.6		72.3
190	20.1					50.3				
260		25.2		29.15			63.0		72.9	
310	22.5					56.3				
330		26.5					66.3			
360		26.65	28.45		32.1		66.6	71.1		80.3
410	23.9		59.3			59.3				
430		28.3	32.1	32.15	33.15		70.8	80.3	80.4	82.9
530	25.15					62.9				
690		30.5	34.0	34.55	35.3		76.5	85.0	86.4	88.3
780	26.65					66.6				
840		32.0					80.0			
1380	29.2					73.0				
1980	30.4					76.0				

CONCLUSIONS.

The foregoing results lead to the following conclusions :

1. The speed of the reaction is influenced to a marked de-

VL



gree by the temperature, the speed increasing with rise of temperature.

2. The presence in the mixture of an excess of one or more of the components increases the speed. The effect of an excess of potassium iodide is about the same as an equivalent excess of potassium chlorate. But a corresponding excess of acid causes a greater increase of speed.

3. Other things being equal the speed of the reaction is modified by the degree of concentration of the mixtures, the speed increasing with the concentration.

4. To obtain the complete reduction of potassium chlorate by potassium iodide and hydrochloric acid in a comparatively short time, the solutions must be concentrated, there

must be present quite an excess of both potassium iodide and hydrochloric acid, and the mixture must be strongly heated.

5. The presence of an excess of the ordinary inorganic acids accelerates the reaction. Assuming their respective influences as indicating their relative strengths,¹ the results on acceleration show the following order of strength: (1) hydrobromic, (2) hydrochloric, (3) nitric, and (4) sulphuric.

ON THE EXISTENCE OF THE SULPHOXYANTI-MONiates.

BY LEROY W. McCAY.

The recent appearance of Dr. Bohuslav Brauner's paper on the action of hydrogen sulphide on solutions of antimonious acid² induces me to publish the following preliminary notice respecting my own work on the same subject.

Rammelsberg's Salt.

In the year 1841, in an article upon the sulphantimoniates and sulpharseniates,³ Rammelsberg described a remarkable salt which he obtained by treating pentasulphide of antimony with cold, moderately concentrated potassium hydroxide. The potassium metantimoniate which separated out as a heavy white powder on treating the pentasulphide of antimony with potassium hydroxide was removed by filtration, and the filtrate concentrated by evaporation. The hot liquid thus obtained yielded on cooling long, needle-shaped crystals of a colorless salt which bore no resemblance to the ordinary potassium sulphantimoniate. The following is Rammelsberg's analysis:

Potassium	23.400 ⁴
Antimony	37.803
Sulphur	18.195
Oxygen	7.298
Water	13.304

100.000

¹ These acids are arranged in the same order by Ostwald, who investigated the influence of their presence on the speed of the reduction of bromic acid by hydriodic acid: *Ztschr. phys. Chem.*, **2**, 135, (1888.) It was also found that organic acids and boric acid do not increase the speed.

² *J. Chem. Soc.*, **67**, 527 (1895).

³ *Ann. der Phys. Pogg.*, **52**, 193.

⁴ His second determination of potassium. I take this figure rather than the other (22.60) because it makes the results found agree better with those demanded by theory.

Rammelsberg regarded the compound as a double salt, and wrote its formula $2(\text{K}_2\text{SbS}_4) + 9\text{H}_2\text{O} + 2(\text{KSbO}_3) + \text{H}_2\text{O}$. A salt having such a composition would, according to Rammelsberg, require :

Potassium	23.002
Antimony	37.863
Sulphur	18.889
Oxygen	7.043
Water	13.203
	<hr/>
	100.000

It will be observed that these percentages agree remarkably well with those found.

The peculiar composition of the salt did not fail to surprise Rammelsberg. In discussing the matter he states definitely that it is, with one exception,¹ the only compound of the kind known to the chemist.

The results of my study of the action of sulphuretted hydrogen on solutions of antimonious acid—a matter which has engaged my attention more or less ever since the appearance of my paper on the action of sulphuretted hydrogen on solutions of arsenious acid²—have led me to believe that the salts of sulphonyantimonous acid are capable of existing. I have felt convinced for a number of years that the formation of the mixture of antimony pentasulphide, antimony trisulphide and sulphur which, under ordinary circumstances, is always formed when sulphuretted hydrogen is permitted to bubble through acidified solutions of antimonious acid, can be explained in a manner perfectly analogous to that in which the mixture of arsenious pentasulphide, arsenious trisulphide and sulphur is accounted for when sulphuretted hydrogen acts on acidified solutions of arsenious acid. A great deal of work, however, satisfied me that it would be impossible to solve the problem by merely considering the products formed during the interaction of the sulphuretted hydrogen and antimonious acid under different circumstances; consequently I decided to make a number of experiments with the view of settling defi-

¹ Berzelius has described a salt of tungsten to which he assigns the formula $\text{K}_2\text{WS}_4 + \text{K}_2\text{WO}_4$.—*Traité de Chimie*, 2 Ed., III, p. 197.

² This JOURNAL, 10, 459.

nitely whether the salts of sulphoxyantimonic acid could be prepared.¹ By examining into the properties and reactions I hoped to obtain an insight into the mechanism of the changes which, until recently,² have been fully as mysterious as those relating to the interaction of sulphuretted hydrogen and arsenic acid used to be.

It was while endeavoring to prepare the barium salt of monosulphoxyantimonic acid, that I ran across the article of Rammelsberg above referred to. A mere glance at the formula proposed by him for this double salt persuaded me that it was one of the suspected sulphoxyantimoniates—not the particular one I was looking for, but still a sulphoxy compound. It will be seen that the dualistic formula $2(K_3SbS_4) + 9H_2O + 2(KSbO_3) + H_2O$ can be written $K_4Sb_2O_3S_4 + 5H_2O$ —*i. e.*, we can regard the compound as a sulphoxy salt of the pyro form. Using the more recent atomic weight determination³ in the calculation, a salt of this composition would require :

K ₄	23.59
Sb ₂	36.27
O ₃	7.24
S ₄	19.33
5H ₂ O	13.57
	<hr/>
	100.00

These figures are practically the same as those found by Rammelsberg. But another possibility suggests itself. The Rammelsberg salt can be regarded as a secondary potassium orthodisulphoxyantimoniate, $K_2HSbO_2S_2 + 2H_2O$. Since the days of dualism are about past, and our modern conceptions concerning the make-up of double salts are quite different from those in vogue when Rammelsberg published his article on the sulphantimoniates and sulpharseniates, the ideas here thrown out would seem to be perfectly reasonable.

Preparation of the Salt.

The matter is one of intense interest, and inasmuch as a proof of the existence of the sulphoxyantimoniates would, as before

¹ According to Feit and Kubierschky the sulphoxyantimoniates are incapable of existing at ordinary temperatures.—*Ber. d. chem. Ges.*, **21**, 1660.

² Brauner: *Loc. cit.*

³ Classen: *Quant. Anal. Chemie*, 3te Aufl. Also Sb = 120.

intimated, serve to cast a great deal of light upon, if not completely account for, the peculiar conduct of antimonious acid when treated with sulphuretted hydrogen, it seemed wise to repeat Rammelsberg's experiments and examine the salt in detail. A revision of his work appears all the more desirable when we consider the fact that over half a century has elapsed since the attention of the chemical world was called to the existence of the salt.

I.—Pentasulphide of antimony, prepared by precipitating a solution of Schlippe's salt with sulphuric acid, was washed, dried, and treated with a sufficient amount of cold, moderately concentrated potassium hydroxide to produce complete decomposition. After standing about twenty-four hours, the dirty, white precipitate of potassium metantimoniate was filtered off, and the filtrate, in a porcelain dish, evaporated on the water-bath until signs of crystallization were observed. The source of heat was now removed, the dish with its contents placed in a cool spot and the crystallization allowed to proceed. In the course of twelve hours there had separated out a number of semispherical aggregates made up of needle-shaped crystals grouped in concentric radiating clusters. The diameters of some of the aggregates were fully one centimeter. The mother-liquor was poured off, and the crystals freed as far as possible from that adhering to them by first bringing them into a large Gooch crucible made of platinum, connecting this in the ordinary way with the water-pump, and sucking them until all spraying at the bottom of the crucible had ceased. They were then pressed again and again between folds of filter paper until they no longer stained the same, and finally dried in a vacuum over caustic lime. They were of a straw-yellow color. The following are the results of my analysis of the salt:

Potassium	23.10
Antimony	36.97	36.60
Oxygen
Sulphur	18.64
Water	13.79

The percentages are to all intents and purposes the same as those found by Rammelsberg.

The salt could be kept for a long time in a vacuum over

caustic lime without undergoing decomposition, but in the air, especially when this was moist, the crystals soon became sugar-brown, then red, and finally crimson. They did not, however, deliquesce or crumble to pieces, but apparently remained dry, and, as far as form was concerned, intact. When freshly prepared the salt was completely soluble in water, but when it had become reddish there was always a small residue which refused to dissolve. This residue appeared to be sulphide of antimony.

II.—In order to obtain a larger quantity of the salt, I treated 64 grams of antimony pentasulphide (Golden Sulphur—Merck & Co.) in an Erlenmeyer flask of about 650 cc. capacity, with 46 grams of potassium hydroxide (87.4 per cent. KOH) dissolved in 250 cc. of water. The flask was corked, violently shaken every now and then, and allowed to stand in a cool place for twenty-four hours. The potassium metantimoniate was filtered off, and the reddish filtrate evaporated in a large porcelain dish on the water-bath until signs of crystallization appeared. The source of heat was now removed and the crystallization allowed to proceed on the bath. The yield here was much larger than in the first case. There were no semispherical aggregates formed; the crystals separated out more as individuals, and they were longer and thicker than those first obtained. Some were as long and as thick as an ordinary pin. The mother-liquor was removed and the salt dried as described under I. The above quantities of antimony pentasulphide and potassium hydroxide were used because it seemed probable that the salt might be formed in accordance with the equation

$2\text{Sb}_2\text{S}_5 + 9\text{KOH} = \text{K}_2\text{HSbO}_2\cdot\text{S}_2 + \text{KSbO}_3 + 2\text{K}_3\text{SbS}_4 + 4\text{H}_2\text{O}.$ ¹
On concentrating the filtrate a second crop of crystals was obtained.

Analyses.

Potassium	23.01
Antimony	36.69	36.97
Oxygen
Sulphur	18.38	18.57
Water	13.27	13.38	13.22

¹ $2\text{Sb}_2\text{S}_5 + 9\text{KOH} = 3\text{K}_2\text{HSbO}_2\cdot\text{S}_2 + \text{K}_3\text{SbS}_4 + 3\text{H}_2\text{O}.$ A portion of the salt, however, owing to its instability, decomposes, splitting up into potassium metantimoniate and potassium sulphantimoniate: $2(\text{K}_2\text{HSbO}_2\cdot\text{S}_2) = \text{KSbO}_3 + \text{K}_3\text{SbS}_4 + \text{H}_2\text{O}.$

Secondary Potassium Orthodisulphoxyantimoniate.

The question now arises, what is this salt? As I have indicated, there are three possibilities. It is either (a) a double salt, (b) pyrosulphoxy salt, or (c) a secondary orthodisulphoxyantimoniate. The chance of its being a double salt in the Rammelsberg sense is extremely improbable, for from our modern standpoint a dualistic conception in regard to the composition of a compound is scarcely permissible when its constitution can be as well expressed by means of a unitary formula. If we define a double salt to be a polybasic acid in which the hydrogen is partly or wholly replaced by equivalent amounts of two metals, the compound in question will be removed at once from the class of double salts. This must be so for the salt contains but one metal. This fact, along with the occurrence together in a compound of an oxy- and sulpho-acid of the same element, puzzled Rammelsberg, and he is very careful to point out that, with one possible exception,¹ the phenomenon is unique. Is it a pyrosulphoxy compound? We have no definite means for deciding against this view, but there is no reason why we should assign to the salt the more complex pyro structure when the facts can be equally well accounted for by regarding it as a simple ortho compound. The salt exhibits the characteristics of a sulphantimoniate far more than it does those of an oxyantimoniate. As far as I can discover, no pyrosulphantimoniates have ever been prepared, whereas the ortho compounds are well known; hence it would be gratuitous to write the formula for the salt $K_4Sb_2O_3.S_4 + 5H_2O$. When heated it acts precisely as a secondary salt might be expected to behave. At 110° it loses very little water,—only a few milligrams. When kept, however, for two hours at 150° , four-fifths of its water escapes. At 250 – 260° the last traces are evolved and the salt is yellow and anhydrous. As proof of my statement I offer the following determinations of the water in a sample of the salt:

0.8474 gram of salt was kept at a temperature of 145 – 150° for two hours and then weighed. It was again placed in the air-bath and kept at 145 – 160° for one and a half hours. The

¹ Berzelius' $K_2WO_4 + K_2WS_4$ is undoubtedly a sulphyoxytungstate, $K_2WO_2.S_2$. I hope to examine this salt soon.

weight remained constant. The loss amounted to 0.0888 gram = 10.48 per cent. H_2O . It was now heated to $250-260^\circ$ and kept at this temperature until the weight remained constant. The loss equalled 0.0232 gram = 2.74 per cent. H_2O . $10.48 + 2.74 = 13.22$ per cent. H_2O , while theory demands 13.57. The determination was made a second time with 0.8407 gram salt. At $145-150^\circ$ it lost 10.68 per cent. H_2O ; and at $250-260^\circ$, 2.70 per cent. H_2O . $10.68 + 2.70 = 13.38$ per cent. H_2O .

Assuming then that the water which escapes at $140-150^\circ$ is water of crystallization, while that evolved at $250-260^\circ$ is water of constitution, the simplest and most consistent formula we can assign to the compound is unquestionably $\text{K}_2\text{HSbO}_2\cdot\text{S}_2 + 2\text{H}_2\text{O}$. In other words it is the secondary potassium salt of orthodisulphoxyantimonic acid.¹

Calculated for $\text{K}_2\text{HSbO}_2\cdot\text{S}_2 + 2\text{H}_2\text{O}$.			Found.				
K ₂	78.06	23.59	23.01
H	1.00	0.30	0.30	0.30
Sb	120.00	36.27	36.69	36.97
O ₂	31.92	9.65
S ₂	63.96	19.33	18.38	18.57
2H ₂ O	35.92	10.86	10.68	10.48
	<hr/>	<hr/>					
	330.86	100.00					

Reactions.

The hydroxides of the alkaline earth metals produce in aqueous solutions of the salt white precipitates which on standing become crystalline. Silver nitrate gives a jet black, copper sulphate a dark red, and lead acetate a cherry-red precipitate. The latter two precipitates become black on standing. The precipitates do not appear to be sulphy compounds. If an aqueous solution of the salt be treated with a few drops of acetic acid a very small amount of sulphuretted hydrogen is evolved; the liquid becomes orange in color, but it remains perfectly clear for days. If the flask containing the solution be corked immediately after the addition of the acid, and well shaken, the sulphuretted hydrogen evolved is soon absorbed, and so completely that the atmosphere of the

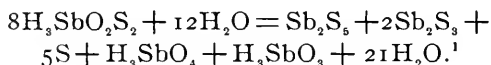
¹ K. Preis has prepared the tertiary sodium salt of orthodisulphoxyarsenic acid, $\text{Na}_3\text{AsO}_2\cdot\text{S}_2 + 10\text{H}_2\text{O}$. Ann. Chem. (Liebig), **257**, 184.

flask is without action on acetate-of-lead paper. When hydrochloric acid is added to a solution of the salt, a mixture of antimony pentasulphide, antimony trisulphide and free sulphur, along with some antimony pentoxide and antimony trioxide is precipitated, while small amounts of antimony pentoxide and antimony trioxide remain in solution. The more acid is added, care being taken not to add enough to attack the sulphides, the more pentoxide and trioxide remain dissolved. In this case also traces of sulphuretted hydrogen escape, but if the experiment be conducted in a closed flask which is occasionally well shaken the gas is after a short time completely absorbed.

In my qualitative study of the action of acids on solutions of the salt, I proceeded as follows : The salt (about one gram) was placed in a small flask, dissolved in water (100 cc.), hydrochloric acid (5-10 cc.) added, and the flask corked and violently shaken. After standing until the supernatant liquid was clear, the red precipitate was filtered off, washed thoroughly with water to remove the hydrochloric acid, and then again and again with alcohol and carbon bisulphide. The alcohol and carbon bisulphide washings were collected separately and evaporated. A residue of sulphur remained. The red precipitate, now free from sulphur, was extracted with a strong solution of tartaric acid and then washed with water to remove this. The tartaric-acid extract proved on further examination to contain considerable quantities of the pentoxide and trioxide. Since relatively large amounts of sulphur were removed by the alcohol and carbon bisulphide, the red precipitate must of course have contained antimony trisulphide. The fact that the red precipitate after the various washings always dissolved in strong hydrochloric acid with separation of sulphur proved that it also contained antimony pentasulphide. One part of the original filtrate from the red precipitate was tested for antimony pentoxide with potassium iodide, according to Bunsen's method. On the addition of a few crystals of this salt to the liquid it became reddish-brown. To the other portion silver nitrate¹ in excess was added, then

¹ In making this test of Rose, the formation of silver chloride does not seem to interfere in the least with the reaction, provided one uses enough of the reagents—especially of ammonia.

potassium hydroxide and finally ammonia. A heavy black precipitate insoluble in ammonia separated out, showing the presence of antimony trioxide. The sulphoxyantimonic acid then, set free upon the addition of a mineral acid to an aqueous solution of the Rammelsberg salt, undergoes decomposition at once, and apparently according to the following scheme:



Of course a great deal will depend upon the strength of the salt solution, the concentration of the mineral acid, and the temperature, but the equation will serve to give a fair idea of the reaction. The presence of antimony pentoxide in the red precipitate and in the filtrate from it is a matter in regard to which I am not quite clear. Judging from what occurs in the corresponding case of the sulphoxy compounds of arsenic, one would expect only a separation of the trioxide.² I am devoting much time to a study of this remarkable reaction, and will reserve a further discussion of it for a future time when I hope to publish the results of my examination of the action of sulphuretted hydrogen on acid solutions of antimonic acid. In the light of the elaborate and excellent work recently done by Dr. Brauner and that shed on the subject by the above considerations in regard to the existence of the sulphoxyantimoniates, the action of sulphuretted hydrogen on antimonic acid solutions can no longer be regarded as a mystery.

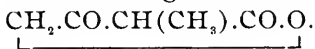
¹ I venture to predict that the orthodisulphoxyantimonic acid first splits up into orthomonosulphoxyantimonic acid and sulphuretted hydrogen, and that it is owing to the interaction of these two compounds along with water that the complex mixture of sulphides, oxides and sulphur is due: $8\text{H}_3\text{SbO}_2\text{S}_2 + 12\text{H}_2\text{O} = 8\text{H}_3\text{SbO}_3\text{S} + 8\text{H}_2\text{S} + 4\text{H}_2\text{O}$.

² Michaelis, however, has proven that orthomonosulphoxyphosphoric acid splits up as follows: (1) $\text{H}_3\text{PO}_3\text{S} + \text{H}_2\text{O} = \text{H}_3\text{PO}_4 + \text{H}_2\text{S}$, and (2) $\text{H}_3\text{PO}_3\text{S} = \text{H}_3\text{PO}_3 + \text{S}$.—*Ber. d. chem. Ges.*, **5**, 4.

TETRINIC ACID.

BY PAUL C. FREER.

A paper on the constitution of tetrinic acid by Louis Wolff¹ has just appeared, and in it the author reaches the conclusion that the acid is a lactone having the structure



This view agrees with that previously expressed by Michael² and by Cornelius and Moscheles,³ although formerly direct proof that the acid was really a lactone (*i. e.*, that it did not contain a carboxyl group) was only to be found in one experiment by Moscheles and Cornelius, showing that ethyl tetrinate could be dissolved in hot caustic soda and could be separated therefrom unchanged on acidifying. Wolff, however, has shown in his latest paper that the solid anilide of tetrinic acid is easily reduced to phenylamido- α -methylbutyrolactone, so that the lactone-structure of the original body is thereby rendered more probable. A number of formulæ have been suggested for tetrinic acid, which were based on the assumption that this substance had twice (Nef⁴) or three times (Demarcay)⁵ the molecular-weight assigned to it by Cornelius and Moscheles, Pawlow⁶, Michael, or Wolff.⁷ As yet, there has appeared but one molecular weight determination of a homologue of this body. The molecular weight of ethyl pentinate was obtained by Moscheles and Cornelius⁸ in a solution of glacial acetic acid according to Raoult's method, and agreed with the formula $\text{C}_8\text{H}_{12}\text{O}_3$. On the other hand a vapor-density of ethyl tetrinate taken in the vapor of diphenylamine gave figures agreeing more closely with $\text{C}_{14}\text{H}_{20}\text{O}_6$. These results are not conclusive, for it is easily conceivable that dissociation of ethyl pentinate (provided it were to have a double molecular weight) might take place on solution in such a medium as glacial acetic acid, with a resulting lowering of the molecular weight. In none of

¹ Ann. Chem. (Liebig), **288**, 1.

² J. prakt. Chem., **37**, 502.

³ Ber. d. chem. Ges., **21**, 2603.

⁴ Ann. Chem. (Liebig), **266**, 90.

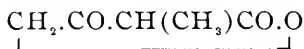
⁵ Ann. Chim. Phys. [5] **20**, 433; Bull. Soc. chim. (Paris), **33**, 516.

⁶ Ber. d. chem. Ges., **16**, 486, 1871; **18**, Ref., 182.

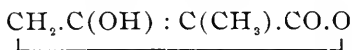
⁷ Ann. Chem. (Liebig), **260**, 87.

⁸ Ber. d. chem. Ges., **27**, 243.

Wolff's work is there any direct proof of the simpler formula $C_6H_6O_3$ of tetrinic acid, yet when we consider the peculiarities of tetrinic acid (such as its high melting and boiling-points), it is evident that the true molecular weight should be definitely settled, before the decomposition products of the acid can be regarded in their proper aspect. If tetrinic acid were to have a lactide formula similar to that suggested by Nef, it is very easily conceivable that the various reagents used to decompose the same would give bodies which would equally well agree with this or with the simpler lactone constitution. In many respects tetrinic acid is a most peculiar body, whose properties are entirely at variance with what we should expect those of a substance of the structure



to be. Especially prominent are the intensely acid properties which are made apparent by Walden¹ in his study of the electric conductivity of solutions of tetrinate of sodium, for he found the avidity of tetrinic acid to be five times that of the monobasic fatty acids, and besides, it is a well known fact that tetrinic acid easily decomposes carbonates. Such properties are not, however, those of ordinary ketones. They would be more intelligible were tetrinic acid to possess the formula



which was assigned to it by me², or if it were to have that given it by Nef³ or originally by Wolff.⁴

Because of these contradictory properties, and also, if possible, to strengthen my former views, I have from time to time continued my investigation of tetrinic acid and, as a result, I can come to no other conclusion than that at which I originally arrived. Owing to the recent paper by Wolff, I have decided to publish the results which I now have, and then to leave the field to my German colleague. I have the more right to do so, as my conclusions differ from his, and as none of my work has been parallel or in contact with his own.

In studying the structure of tetrinic acid, it is of primary

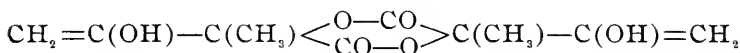
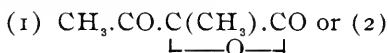
¹ Ber. d. chem. Ges., **24**, 2029.

³ Ann. Chem. (Liebig), **266**, 92.

² This JOURNAL, **13**, 311.

⁴ *Ibid.*, **260**, 87.

importance thoroughly to understand the chemical nature of the monobrom derivatives of methyl acetoacetic ester. Nef¹ maintains that brommethylacetoacetic ester is an α -substitution-product because, by the action of bromine on sodium methylacetoacetic ester or on the free substance, he has obtained an oil which boils constantly at 107° (30 mm.), which gives analytical results in accord with theory, does not dissolve in aqueous alkalis, is not changed by cold nitric acid, and which, he says, changes to tetrinic acid and ethyl bromide, quantitatively on heating for six hours at 100° . Basing his views on the supposition that here there is in reality α -brommethylacetoacetic ester, he maintains that the only possible formula for tetrinic acid is either



and of these he favors the latter.

Wolff has in his recent article shown beyond a doubt that tetrinic acid is really a γ -lactone, or a derivative, for he obtained $\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2\text{OH}$, (ethyl ketol) and glycolic and propionic acids as decomposition products on heating with water and baryta respectively, and in addition reduced the anilide of tetrinic acid to phenylamido α -methylbutyrolactone.

This author, however, does not doubt that α -brommethylacetoacetic ester is the original source of the acid, and explains its formation by assuming a molecular rearrangement before the separation of ethyl bromide, such as Hantzsch² has shown to be the case with α -bromacetoacetic ester under the influence of hydrobromic acid.

The Action of Bromine on Methylacetoacetic Ester and its Sodium Derivative.

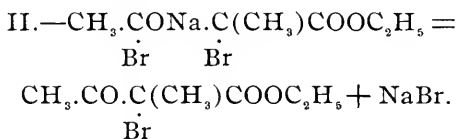
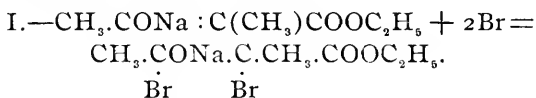
I have subjected the action of bromine on methylacetoacetic ester to a careful revision, and have come to conclusions which differ from those of Nef in many particulars. In his paper³ Nef says that on treating sodium methylacetoacetic ester with one molecule of bromine, no trace of hydrobro-

¹ Ann. Chem. (Liebig), **266**, 90.

² Ber. d. chem. Ges., **27**, 3168.

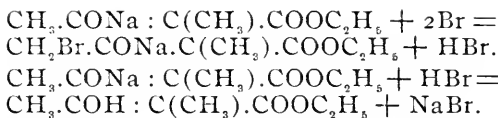
³ Ann. Chem. (Liebig), **266**, 62.

mic acid is developed, as is the case with sodium acetoacetic ester. If this is so, the resulting monobrommethylacetoacetic ester would necessarily have to be an α -substituted product, as the following reaction will show :



If, on the other hand, it can be shown that hydrobromic acid really is developed, then it is equally certain that a γ -product must at least in part be obtained. If, now, sodium methylacetoacetic ester, suspended in absolute ether, is treated with one-half the calculated quantity of bromine, there is found in the ethereal solution separated by filtration an oil which consists mainly of free methylacetoacetic ester, mixed with a minor quantity of the brominated product,¹ while a considerable quantity of tetrinic acid, in a very impure state, is left in the retort after distillation. On the other hand, if one molecule of bromine is used, there results a product which contains no unchanged methylacetoacetic ester, but which distils much as Nef describes with the exception that the product has no absolutely constant boiling-point, and leaves a considerable residue of impure tetrinic acid. The formation of free methylacetoacetic ester, however, shows that hydrobromic acid must have been present during the first part of the reaction, and that as a consequence γ -methylacetoacetic ester must, at least in part, have been formed. The action of bromine on sodium methylacetoacetic ester must therefore have been partly one of direct substitution, with separation of hydrobromic acid, as follows :

¹ From 72 grams of Kahlbaum's methylacetoacetic ester, the sodium derivative of which I prepared according to Nef's directions, I obtained 26 grams of fractioned methylacetoacetic ester (B. P., 88-91°; 30 mm.), which I afterward brominated and converted into tetrinic acid. From a second sample (48 grams) of pure methylacetoacetic ester, prepared by myself, I regained 8 grams of impure methylacetoacetic ester—a relatively smaller quantity than the above—and in this case I obtained no residue of tetrinic acid. This experiment will be described further on.



In brominating free methylacetoacetic ester I have come upon remarkable results. I carefully purified a sample which I had obtained from Kahlbaum by shaking several times with a dilute sodium-hydroxide solution, drying and then fractioning into two portions, one boiling at 84–85° (25 mm.) and the other 85–87° (25 mm.). 11 grams of the 84–85° body was dissolved in 3 volumes of pure chloroform, cooled with ice-water and then brominated with the calculated quantity (15.5 grams) of bromine. The chloroform and hydrobromic acid were then evaporated in the cold in a vacuum, and the resulting oil fractioned. The greater part passed over between 107° and 112° (30 mm.), and there remained 1.1 grams of tetrinic acid in the flask. I could obtain no perfectly constant body from the oil, but the portion boiling between 107° and 112° (30 mm.) gave analytical results agreeing with monobrommethylacetoacetic ester. Quite different results were obtained from the methylacetoacetic ester which passed over between 85° and 87°. Of this substance I brominated 11 grams in the same way, and after removing chloroform and hydrobromic acid as before, I fractioned at 30 mm. pressure. When the temperature of the oil-bath had reached 120°, the pressure suddenly fell to 70 mm., a violent ebullition of ethyl bromide took place and the contents of the flask became solid. The distillation was carried on until the oil-bath reached 142°, when one-third had passed over, and partly solidified in the receiver. The remainder in the flask consisted of 4 grams of pure tetrinic acid. On brominating 56 grams of the Kahlbaum ester, which had not been separated by fractionation, a similar result was obtained. When the oil-bath was heated to 100°, 30 mm. pressure, nothing but a little chloroform and ethyl bromide had passed off. The pressure then suddenly sank to 100 mm., a violent ebullition of ethyl bromide took place, and the contents of the distilling-flask solidified, yielding 13 grams of pure tetrinic acid. This was filtered off and the mother-liquors were then fractioned, when they passed over between

107° and 110° without forming any more tetrinic acid. As all of these results were obtained under the same conditions, I came to the conclusion that the difference lay in a difference between the two fractions of methylacetoacetic ether (84–85° and 85–87°, 25 mm.). I therefore prepared 250 grams of methylacetoacetic ester in the laboratory, taking every precaution to obtain a pure product, and removing any unchanged acetoacetic ester by extraction with dilute sodium hydroxide. This product I carefully fractioned and separated into two portions, one boiling constantly at 107° (49–50 mm.), and the other which consisted only of about 30 grams, between 108 and 109° (50 mm.). 60 grams of the first product were dissolved in 5 volumes of chloroform, placed in a freezing-mixture and the calculated quantity of bromine, dissolved in chloroform, slowly added under constant stirring. The resulting solution was shaken with water to remove hydrobromic acid, dried over calcium chloride, and the chloroform then removed at 30° by distilling under reduced pressure. The remaining colorless oil was then fractioned under 30 mm. pressure. The entire substance, excepting 5 grams, then passed over between 107° and 111°, and no tetrinic acid was left in the retort. This result was therefore radically different from that obtained with the Kahlbaum methylacetoacetic ester, and a repetition brought about the same result. The major portion of the oil (54.1 grams) distilled between 107° and 109° (30 mm.), and a lesser amount (7 grams) between 109° and 111°, while 5 grams went over between 111° and 120°. The bromination-product has not, therefore, an absolutely constant boiling-point. The product (107–109°) on refractioning also separates into a higher and lower fraction. I have never obtained the oil which Nef describes, boiling constantly at 107° (30 mm.), although I took every precaution to have a constant boiling methylacetoacetic ester and varied the bromination in every way. Bromine determinations of each fraction, beginning with the lowest, show a steadily increasing amount of bromine from 26.5 per cent. up, but never exceed the quantity calculated for monobromomethylacetoacetic ester, in fractions below 111°. The result is scarcely different if the methylacetoacetic ester is brominated at ordinary temperatures, and if

the hydrobromic acid is removed by evaporation in a vacuum, although in the latter event more high-boiling oil and some tetrinic acid are obtained on distillation. There is, therefore, a radical difference between the behavior of the Kahlbaum methylacetoacetic ether and that prepared by the usual method in the laboratory, the one promptly yielding a large quantity of tetrinic acid when the distilling flask is heated to 100° , while the other distills with but little decomposition. In no event, however, is an absolutely constant-boiling oil obtained. A very large proportion, it is true, passes over between 107° and 109° , with the thermometer remaining stationary for some time at 108.5° (30 mm.)¹, but a considerable part of the bromination-product boils from 109 to 111° , and another part from 111° to 125° , the high-boiling residue passing over up to 150° . The high-boiling fractions (125 – 145°) contain more bromine² than is required for monobrommethylacetoacetic ester, and hence consists largely of dibrommethylacetoacetic ester. Some unchanged methylacetoacetic ester passes over below 100° , showing that a portion of the bromine is used to form the dibrom product. In brominating methylacetoacetic ester, with the calculated quantity of bromine, therefore, a portion of the bromine attacks the ester, which is already substituted, while a part of the substance remains unaffected.

The product boiling at 107.5° to 108.5° , as indeed is true of all of the fractions, is instantly attacked by pure bromine (free from hydrobromic acid), if it is not diluted; if, however, it is mixed with five times its volume of pure chloroform, the action of bromine is extremely slow; one drop of bromine, added to five grams so diluted, remains unchanged for several hours, but if the mixture is allowed to stand over night, bromination takes place, until finally the calculated quantity for the formation of a dibrom product can be added. The resulting colorless oil, when washed with water, dried over calcium chloride and distilled, boils at 144° (25 mm.), and is undoubtedly dibrommethylacetoacetic ester.

¹ I was very careful to use an absolutely correct manometer, the pressure in which and in all subsequent distillations, unless otherwise stated, was kept constantly at 30 mm. The thermometer in the distilling-flask was entirely in the vapor of the distillate and the oil-bath was kept constant at 128° .

² An analysis of this portion shows 45.66 per cent. bromine, calculated for dibrommethylacetoacetic ester, 52.9 per cent.

The Action of Sodium on Monobrommethylacetoacetic Ester.

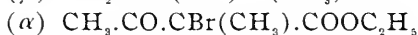
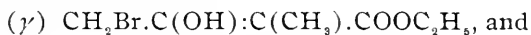
30 grams of monobrommethylacetoacetic ester were dissolved in 8 times the volume of absolute ether, and then the calculated quantity of sodium (3.1 grams) in the form of fine wire was added. A reaction, *accompanied by the evolution of hydrogen*, at once set in, increasing in violence so that the flask had to be kept cool. After two hours all of the sodium had disappeared, the solution had become brown in color, and a brownish yellow precipitate had separated. The precipitate was removed by filtration. It had an alkaline reaction when added to water,¹ and on acidifying a brown oil separated. The filtrate was also acidified, washed with water and dried over calcium chloride. The two products were then fractioned separately, under 30 mm. pressure, but gave substantially the same result. About one-third passed over below 90°, and consisted of regenerated methylacetoacetic ester; the next portion, less in quantity, contained unchanged brommethylacetoacetic ester; and after this had passed over the thermometer rapidly rose to 200°, and a thick oil distilled which could not be crystallized, and from which no constant boiling product could be obtained. It is neutral and colors a solution of ferric chloride a deep red. Probably this substance is related to succinylosuccinic ester, but its small yield and uninviting properties caused me to forego further investigation. The formation of hydrogen by the action of sodium shows that γ -brommethylacetoacetic ester must have been present.

Oxidation of Brommethylacetoacetic Ester.

Brommethylacetoacetic ester, when covered with a dilute solution of sodium carbonate is instantly oxidized by a solution of potassium permanganate. 19 grams of brommethylacetoacetic ester (boiling-point 108.5°) was mixed with a solution of 9 grams of sodium carbonate in 150 cc. of water, and then 20 grams of potassium permanganate, dissolved in one liter of water, was slowly added, with constant stirring. When the reaction was complete the manganese dioxide was filtered out and the whole evaporated to dryness. The salts which remained were then repeatedly extracted with hot alcohol,

¹ The precipitate contains a considerable quantity of sodium bromide.

and the alcoholic solution evaporated. Both the undissolved and the dissolved salts were separately examined. The result was that the undissolved portion contained sodium oxalate. Now, if we compare the formulae of the γ - and α -brommethylacetoacetic ester—



—it is evident that oxalic acid can be produced only by the former, which primarily should give bromacetic acid or glycolic acid, which, owing to the ease with which it is oxidized, would subsequently change to oxalic acid. From the α -brom ester, on the other hand, only acetic acid could be expected. The brommethylacetoacetic ester under investigation, therefore contained γ -brommethylacetoacetic ester.

The portion of the salts produced by oxidation, and which was soluble in alcohol consisted mainly of acetate of sodium, mixed with very little carbonate. This mixture was boiled with a little animal charcoal, filtered and the filtrate treated with a solution of lead acetate. A flocculent precipitate is formed, which soon becomes white and crystalline. This precipitate was carefully separated, washed with water and then decomposed with the aid of hydrogen sulphide. The solution, after filtering out the lead sulphide, was evaporated; a crystalline acid remained, which was very soluble in water and alcohol, which contained halogen, and which in its properties resembled monobromacetic acid. The quantity of this substance was too small for exact identification, but when added to that of the oxalic acid it showed that 1.2 grams of the original brommethylacetoacetic ester must have been the γ -brom derivative. This amounts to about 6 per cent. of the original oil. In order to determine whether the sodium derivative of the methylacetoacetic ester prepared by me behaved like that from the Kahlbaum preparation, I repeated the previous experiment in which I used one-half the calculated quantity of bromine. 48 grams of pure methylacetoacetic ester (B. P. 107.5° at 50 mm.) was converted into the sodium derivative by means of sodium in slight excess, and then carefully brominated with 26.6 grams of bromine. The solid product was then filtered out and washed with pure ether, and

both the ethereal solution and the oil obtained by acidifying the solid were worked up separately. The result was different to some extent from the action on the Kahlbaum product, for, whereas in the former case I obtained on fractioning, a considerable quantity of tetrinic acid in an impure state, in this experiment the oil, both from the ether solution and from the acidified solid boiled with but little residue. The ethereal solution gave an oil which was colorless and all of which passed over between 85° and 111° (30 mm.). On refractioning, I isolated 6 grams below 100° , consisting mainly of regenerated methylacetoacetic ester; 9 grams from 100° to 105° , consisting of a mixture of methylacetoacetic ester and brom-methylacetoacetic ester; 9 grams from 105° to 107° ; 5 grams from 107° to 108° , and 2 grams from 109° to 111° . These results show that there is present a mixture, but that approximately 6 grams of free methylacetoacetic ester were regained. The previous work with the Kahlbaum ester is therefore confirmed, only the product prepared by me gives relatively much less free methylacetoacetic ester, and hence less of γ -brom-methylacetoacetic ester.

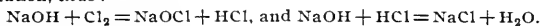
The solid which was left after brominating sodium methylacetoacetic ester and which was separated from the ethereal solution by filtration, was acidified, the resulting oil washed with water, dried and fractioned. It was mainly methylacetoacetic ester (12.5 grams) and a little brommethylacetoacetic ester (1.5 grams). As will be seen, much less than one-half of the methylacetoacetic ester originally used was regained from the solid products of the reaction, although only one-half the calculated quantity of bromine was used in bromination. If the change had taken place entirely according to Nef's view, and no γ -brommethylacetoacetic ester had been formed, then exactly one-half of the methylacetoacetic ester would have been recovered. The loss is accounted for by the fact that the bromine in part substitutes hydrogen in sodium methylacetoacetic ester,¹ that the resulting hydrobro-

¹ It seems probable, from the investigations going on in my laboratory, that the halogens are often capable of directly substituting hydrogen in sodium derivatives, and that the reactions do not always take place by previous addition, with subsequent separation of halhydric acid or metallic halides. The direct substitution of halogen for metal is probably of rare occurrence. Very possibly the production of

mic acid then attacks the sodium methylacetoacetic ester, forming the free compound, while it does not so readily act on the sodium brommethylacetoacetic ester. Sodium brommethylacetoacetic ester does not remain as such, but decomposes and is consequently not regained from the solid product of the reaction, which therefore consists of only one-fourth of the sodium methylacetoacetic ester originally used. A considerable quantity of the brom derivatives must also be found to be present in the ethereal solution which is separated from the solid by filtration for, if the entire reaction were to produce γ -brommethylacetoacetic ester, then there would be enough hydrobromic acid produced to liberate exactly one-half of the methylacetoacetic ester, which latter body would then constitute the entire product to be obtained from the ethereal solution.

Separation of the Brommethylacetoacetic Esters by Alkalies.

As a final proof that the brommethylacetoacetic ester, obtained by direct bromination of pure methylacetoacetic ester is a mixture of α - and γ -brom derivatives, I have extracted an ethereal solution of the pure substance of Nef (boiling at $107-108^\circ$, 30 mm.) with 10 per cent. caustic soda solution, and instantly neutralized the alkali with sulphuric acid. Under these circumstances an oil separates from the alkaline solution, having the properties of brommethylacetoacetic ether, but which, on distillation, gives a higher-boiling product and a considerable residue in the flask. To my surprise, the portion of the oil which was insoluble in alkalies, and which I took to be pure α -brommethylacetoacetic ester, now had a lower boiling-point by two degrees than it had before, and was not perfectly constant. This oil, insoluble in alkali, and which presumably contained only the α -brom product, I carefully fractioned into portions $100^\circ-104^\circ$, $104^\circ-107^\circ$, and $107^\circ-109^\circ$, and heated each portion separately in a sealed tube at 100° for six hours.¹ There was absolutely no change and no sodium hypochlorite from chlorine and sodium hydroxide is a reaction involving direct substitution, thus:



We are at present investigating the action of bromine on sodium phenols, and on sodium ethylate.

¹ The fraction $107-109^\circ$ (nearly pure α -brommethylacetoacetic ester, *did not change in the least* when heated for ten hours. Then the sealed tube was opened and a little dry, gaseous hydrobromic acid added. The oil then solidified completely to tetronic acid on heating to 100° in a sealed tube for twenty minutes.

tetrinic acid was formed. On the other hand, brommethylacetoacetic ester which has not been extracted with alkalies, yields tetrinic acid with more or less readiness under these circumstances. In no event, however, is the yield a quantitative one; thus 12 grams of brommethylacetoacetic ester (boiling-point $107-109^{\circ}$), heated for ten hours at 100° , yielded 2.2 grams of pure tetrinic acid. The mother-liquors, on again heating, gave after six hours 0.3 gram more. On fractioning the residue, it boiled as before between 109° and 111° , with a small portion of a high-boiling residue. The mother-liquor from any of the sealed tubes in which tetrinic acid has been formed on washing with water, before fractioning, give a reaction for hydrobromic acid in the aqueous solution. I also found that brommethylacetoacetic ester, to which I had added some dry hydrobromic acid, was changed into tetrinic acid in a very short time. Brommethylacetoacetic ester also absorbs dry hydrobromic acid very readily. The conclusions which can be drawn from this work are as follows:

1. The product of brominating either methylacetoacetic ester or sodium methylacetoacetic ester with the calculated quantity of bromine is not a uniform body. It consists partly of free methylacetoacetic ester, of α - and of γ -brommethylacetic ester and of dibrommethylacetoacetic ester.

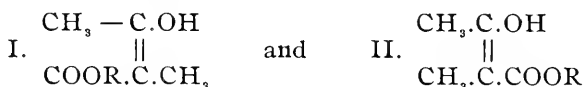
2. Tetrinic acid is quickly formed from γ -brommethylacetoacetic ester, so that the latter cannot be distilled without change.

3. α -Brommethylacetoacetic ester does not change to tetrinic acid when heated to 100° unless hydrobromic acid is present, the hydrobromic acid causing the change by addition.

4. There is a difference between different samples of apparently equally pure methylacetoacetic ester when brominated.¹ I can see no other reason for this difference in behavior than

¹ It is possible, also, that the Kahlbaum ester contains methylacetoacetic methyl ester, which might in part account for the difference between it and my body, yet the quantity of this could scarcely be sufficient to account for all of the tetrinic acid formed from it when its bromine derivative is distilled and, besides, the *higher-boiling* fraction gave relatively the most tetrinic acid when distilled. My acetoacetic ester was pure, for it had an absolutely constant boiling-point. Yet it also gave a brom derivative which, before extracting with alkalies, yielded tetrinic acid on heating to 100° . It would be interesting to repeat the above work, using methylacetoacetic methyl ester.

in the fact that there are two methylacetoacetic esters which are geometrical isomers, *i. e.*—



Formula I would give a γ -brom derivative of the formula $\text{CH}_2\text{Br.C.OH}$

$\begin{array}{c} || \\ \text{COOR.C.CH}_3 \end{array}$, which would readily separate ethyl bromide

and go over into tetrinic acid. This body would therefore be present in the brommethylacetoacetic ester which changes so readily into tetrinic acid at 100° on distillation; the other

γ -brom body, $\begin{array}{c} \text{CH}_2\text{Br.C.OH} \\ || \\ \text{CH}_3.\text{C.COOR} \end{array}$ would only change gradually

through molecular rearrangement. Finally, α -brommethylacetoacetic ester will not produce tetrinic acid at all unless some means are provided to change it first into the γ -brom.¹ This means is found in the action of hydrobromic acid, just as Hantzsch has shown to be the case with α -bromacetoacetic ester. This change, which actually takes place, could easily be explained if α -brommethylacetoacetic ester were to have the formula $\text{CH}_2 : \text{C(OH).CBr(CH}_3\text{).COOC}_2\text{H}_5$, for then it would, on addition of hydrobromic acid, be changed into an addition-product having the structure



which latter body, by separation of hydrobromic acid, would be converted into γ -brommethylacetoacetic ester. However, were α -brommethylacetoacetic ester to have the above structure, it is not easy to see why it does not dissolve in alkalies. It is true that methylacetoacetic ester itself does not dissolve in aqueous alkalies, but one would expect the bromine derivative to be more negative and hence at least as soluble as acetoacetic ester. It must, however, be acknowledged that there are no data at hand to prove that the brom deriva-

¹ The least trace of hydrobromic acid is sufficient to inaugurate the change, which then goes on by separation of hydrobromic acid. In almost all cases unless care has been taken to extract with alkalies, such a trace of hydrobromic acid is present. At temperatures higher than 100° it is formed even from the pure product, and then the production of tetrinic acid goes on.

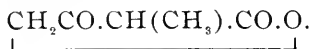
tive should, of necessity, be any more soluble than methyl-acetoacetic ester itself.

In conclusion, I wish to thank Mr. J. E. Whitsit for his conscientious and active assistance in this research.

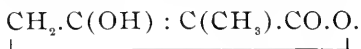
DERIVATIVES OF TETRINIC ACID.

Experimental work by E. R. Miller.

In his recent paper¹ Wolff has investigated a number of decomposition-products of tetrinic acid, produced by the action of water, nitrous anhydride, nitrous acid, and aniline. He comes to the conclusion that the structure of the body is represented by the formula



Some years ago, Freer, by reason of a number of experiments decided that the acid contained an hydroxyl group, and that hence its structure would be thus represented :



There is no reason to change this view at the present time, indeed, were the carbonyl formula for ketones of this acid character not such an unalterable part of the creed of many chemists, they would long ago have recognized the necessity of assuming the hydroxyl formula, for the very proofs which they have been accustomed to advance as absolute in regard to the presence of hydroxyl and the carboxyl group and in the alcohols, have been established with equal certainty for tetrinic acid.

Cornelius and Moscheles have shown that the ethyl ether of tetrinic acid—a neutral body which does not react with phenylhydrazine—can be prepared according to Wedel's² method by the action of hydrochloric acid on an alcoholic solution of tetrinic acid, and Freer prepared the same body by the action of ethyl iodide on the silver salt and showed that the ether so obtained can be readily saponified in the cold, regenerating tetrinic acid. Furthermore, it has been demonstrated in the same place that tetrinic acid, on warming with acetic

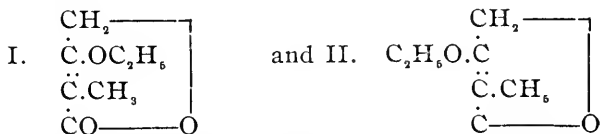
¹ Ann. Chem. (Liebig), 288, 1.

² *Ibid.*, 219, 114.

anhydride, readily yields an acetyl derivative, which dissolves slowly in aqueous potassium hydrate, and from this solution tetrinic acid separates on acidifying, and it will be shown below that similar properties belong to benzoyl tetrinate. Lastly, when we take the stability of sodium tetrinate and its electric conductivity into consideration, there seems to be no doubt as to the hydroxyl group.

One thing still seemed to be necessary in studying tetrinic acid, and that was the definite proof by several methods, that the acid really has the molecular weight assigned to it, and not a double one, as is assumed by Nef, and it was with the object of deciding this point that the investigation of tetrinic acid, begun by Freer, was resumed.

Ethyl Tetrinate.—Tetrinate of silver is, contrary to Demarcay's account, rather soluble in water. A very concentrated neutral solution of potassium tetrinate was precipitated with a concentrated solution of silver nitrate, the precipitated salt filtered, dried on a porous plate, and washed by rubbing in a mortar with water and again filtering,¹ it was finally dried on a porous plate in a vacuum. The resulting perfectly white compound was placed in sealed tubes with one and one-half times the calculated quantity of ethyl iodide and an equal volume of absolute ether. The reaction began in the cold and was finally completed at 80°. The contents of the tube were then filtered and the oil fractioned. By this means, it could be separated into two fractions, one at 175–176° (50 mm.), and the other at 180° (43 mm.) The first fraction remains liquid, but the other becomes solid, melting at 28°. Both the solid and the liquid gave analytical results agreeing with ethyl tetrinate and in accordance with those given by Freer. It seems not improbable that we have here two geometric isomers:



¹ The silver salt must be dried quickly and protected from light, it must not be brought in contact with filter-paper or other organic material, otherwise it rapidly blackens.

but as all attempts definitely to isolate two tetrinic acids have failed, this view is advanced with due caution.

A determination of the vapor-density of ethyl tetrinate was made under diminished pressure (8 mm.) in a large bulb such as is used in the Dumas method, and the result (at 174°) gave for the molecular weight 138.6, calculated 142. There can be no doubt, therefore, that ethyl tetrinate has not a double molecule.

Benzoyl Tetrinate.—20 grams of sodium tetrinate were finely powdered and suspended in 20 cc. of absolute ether, the calculated quantity of benzoyl chloride was then added, and the whole warmed on a water-bath until the odor of benzoyl chloride had disappeared. The ether was then evaporated and the solid residue successively washed with ether, a little alcohol, and finally with water. The resulting benzoyl tetrinate was then dried and recrystallized from pure acetone. It separates in long shiny plates, which melt at 128° . It is slightly soluble in boiling alcohol, being partially decomposed thereby, yielding benzoic ester, and it is also slightly soluble in boiling water.

Calculated for $C_5H_5O_3C_6H_5CO$.		Found.	
		I.	II.
C	66.05	66.07	65.95
H	4.58	4.9	4.9

The molecular weight was taken in benzene solution¹ according to the Beckmann method:

1. Solvent, 19.4098; substance, 0.0970; depression, 0.11° ; $M = 222.6$.

2. Solvent, 21.337; substance, 0.3520; depression, 0.37° ; $M = 218.4$.

Calculated $M = 218$. Benzoyl tetrinate has therefore a molecular weight which agrees with theory.

Benzoyl tetrinate is easily saponified by alcoholic potash. 2 grams of benzoyl tetrinate were digested with a slight excess of methyl-alcoholic potash for several hours. After evaporating the alcohol the residue was slightly acidified with diluted sulphuric acid, filtered, and the precipitate washed with water. The wash-water and the filtrate were examined separately. The precipitate was benzoic acid, and the amount agreed with

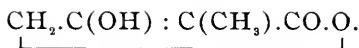
¹ Glacial acetic acid was tried, but it decomposed the benzoyl tetrinate rapidly.

theory (0.938 gram). The filtrate was evaporated to dryness, extracted with alcohol and the alcoholic solution evaporated. It deposited pure tetrinic acid, 1 gram; theory requires 1.045. Benzoyl tetrinate is, therefore, easily saponified to benzoic and tetrinic acids, one molecule of each. Phosphorus pentachloride decomposes benzoyl tetrinate, yielding benzoyl chloride.

β-Chloroxytiglic Lactone : Tetrinic Chloride.—If tetrinic acid is mixed with the calculated quantity of phosphorus pentachloride and a little chloroform is added, so as to bring the reacting bodies in contact, reaction sets in at once, and there results an oil. The latter was freed from phosphorus oxychloride by distillation under diminished pressure, and a yellowish oil which passed over was washed with water, dried over calcium chloride and fractioned. There results a chlorinated body which boils at 106.5–107.5° at 26 mm. pressure, and the greater portion of which solidifies in a freezing-mixture. The solid crystals were filtered from the oil and recrystallized from ether. They form colorless prisms, melting at 30°. The oily portion, upon repeated fractioning, also in part solidifies and, it was discovered, had the same percentage composition as the crystals. This chlorinated body dissolves slowly on warming with caustic alkalis, and hence has the characteristic property of a lactone. Contrary to Demarcay's description, it is perfectly stable and can be kept any length of time without change.

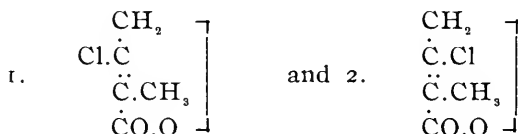
Calculated for $\text{CH}_2\text{CCl} : \text{C}(\text{CH}_3)\text{CO}_2\text{O}$		Found.	II.
C	45.7	45.39
H	3.77	3.87
Cl	26.79	26.5

These results agree with the calculated amounts for tetrinic chloride. The vapor-density of the body determined in the Hofmann apparatus, in the vapor of xylene, gave for the molecular weight, 133.9; calculated molecular weight, 132.5. There can be no doubt from these results that, in the case of tetrinic chloride, as well as in all previous bodies which were studied, the substance is derived from a tetrinic acid of the formula



In his recent paper, Wolff has stated that tetrinic chloride does not exist. It would seem from the above that this statement must be altered.

It is interesting to observe that in the study of tetrinic chloride conditions have been encountered similar to those observed with the ethyl ether of tetrinic acid, *i. e.*, a solid and a liquid tetrinic chloride are present. It seems not improbable, therefore, that here we have the two geometric isomers which are called for by theory, namely :



It would, therefore, be very desirable if work were undertaken with the purpose of isolating the corresponding tetrinic acids. In concluding, I may add that brommethylacetacetic ester, on prolonged heating to 110° , may be brought to yield 87.4 per cent. of the theoretical quantity of tetrinic acid. Hydrobromic acid is always developed during the reaction, as can be shown by passing the gases which are given off through a solution of silver nitrate.

REVIEW.

THE PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. A Manual for the Estimation of Soils, Fertilizers and Agricultural Products. For the Use of Analysts, Teachers and Students of Agricultural Chemistry. Volume I.—Soils. By HARVEY W. WILEY, Chemist of the United States Department of Agriculture. Easton, Pa. : Chemical Publishing Co. pp. 607.

Based upon the fundamental relation of the soil toward all agricultural operations, the careful analysis and classification of soils offered, very early in the history of applied chemistry, an alluring prospect of the possibility of estimating the potentiality of a farm with ease and accuracy. The superficial observer might still wonder why the realization of these hopes is so long delayed. But in fact the analysis of soils for any purpose is of rather limited value and the results, however accurate as applying to the particular sample under examination, will admit of only very carefully drawn conclusions and

rarely of general application. Nevertheless the attention paid to the methods of soil examination is not inconsiderable and there has of late been much progress in this field, in which American investigators make a creditable showing and are freely quoted.

The volume seems to include about all that has been published on the subject of soils of late years. This feature of the work characterizes it to the extent of frequently unduly emphasizing matters of rather secondary importance which may have been much discussed or written about. Soil geology, soil physics, and soil chemistry are treated in considerable detail, particularly the last two. After a discussion of the origin of soils, their geologic characters and a description of the chemical elements involved in their composition, the various operations of their physical and chemical examination are fully treated. Often a number of methods and authorities are cited in detail without leaving with the reader any definite idea as to which is to be preferred or employed. The subject is treated compendiously and not selectively, and this is in some sense a disappointment, since one might have expected to profit by the author's extensive experience in this field. The work is an elaborate summing up of the subject, comprehensive and exhaustive—a reference book; but the treatment is not critical nor is it the crystallization which would best serve as a guide to analytical work. This latter aim was doubtless less in the author's mind, and it can be unreservedly said that he has given us a most valuable work which must to a large extent supplant other treatises of the kind.

A work of this extent can hardly be free of minor features susceptible of criticism, but such examples so far as they occur here, are of secondary importance. The statement that "water is the most important of all plant foods" (p. 6) certainly depends for its accuracy upon the point of view. The terms "early truck" and "truck farming" (p. 249) might be obscure to one not familiar with American dialects; while the effect of reading that the "reduction takes place in a copper erlenmeyer" is startling, to say the least. The photomicrographs of calcium sulphate and magnesium silico-fluoride (Figs. 51 and 52) are evidently interchanged.

The sections devoted to chemical analysis are excellent and particular attention is given to the important subject of the origin and estimation of oxidized nitrogen, even the details of the methods of isolation and study of the micro-organisms of the soil being given.

The work is a notable and important addition to soil literature.

W. E. S.

OBITUARY NOTICES.

LOUIS PASTEUR.

Pasteur died September 28, near Paris. He was born December 27, 1822, at Dôle. In 1843 he entered the École Normale at Paris, and attended the chemical lectures of Balard and Dumas. In his boyhood he had shown marked skill in drawing, and in the field of chemistry at first took special interest in questions of form such as are presented in the phenomena of crystallization. Towards the end of his student career, he repeated, for the sake of the practice, an experimental investigation of de la Provostaye on the crystalline forms of tartaric and racemic acids and their salts. In the course of this work he made the important discovery that racemic acid can be split into two varieties of tartaric acid by crystallizing its ammonium-sodium salt. One of the acids thus obtained, as is well known, is ordinary tartaric acid; the other is a variety that was up to that time unknown. This discovery furnished the foundation of what has since come to be known as stereochemistry. The relations existing between the two varieties of tartaric acid and racemic acid have been shown to exist in many other cases, and these relations have led to the theory of the asymmetric carbon atom, first suggested by Van't Hoff and by Le Bel.

In 1848 Pasteur was called as physicist to the Lyceum of Dijon, and a few months later he accepted the chair of chemistry in the University of Strasburg. In 1854 he became Dean of the Faculty in Lille, and in 1857 he returned to Paris as Director of the École Normale. In 1862 he became a member of the Institute; in 1881 he was elected to the French Academy. In 1874 the National Assembly voted him an annual pension of 20,000 francs. In 1889 he gave up all his public offices in order to devote himself to the management of the famous Pasteur Institute, which was founded by public subscription.

While at Lille, Pasteur took up the study of alcoholic fermentation. His first article on this subject appeared in 1857. In this he showed that fermentation is directly connected with the life and growth of yeast. From this time on, his attention was given largely to the investigation of phenomena produced by minute organisms. He improved the methods used in the manufacture of wines and beers; he discovered the cause of the disease of the silkworm, which threatened disaster to the silk industry of France; and, as all the world knows, he devised methods for combating a number of diseases, such,

for example, as hydrophobia. Pasteur is in fact the father of modern medicine. The methods that he devised for the prevention of chicken cholera and for the treatment of hydrophobia are the methods that seem to promise most success in dealing with many of the diseases of mankind.

I. R.

FELIX HOPPE-SEYLER.

Felix Hoppe-Seyler, renowned not only as a teacher, but also as an investigator in the field of physiological and pathological chemistry, died suddenly August 10, 1895. Although seventy years old, he still retained his vigor and activity as a worker. In 1846 he entered the University of Halle, but shortly afterwards went to Leipsic, where he came in contact with the Weber brothers, Erdmann, Lehmann, and others, all skilled and inspiring instructors, and laid a firm foundation for his future work. The latter part of his student course was spent in Berlin, where he took the degree of Doctor of Medicine in 1850. After practicing medicine for a short time, he was appointed Privatdocent in the University of Greifswald, and two years later returned to Berlin as assistant to Virchow. In 1861 he was appointed to the chair of applied chemistry in the University of Tübingen. He resigned in 1872 to accept the professorship of physiological chemistry in the new University of Strasburg.

Hoppe-Seyler's early researches were upon the structure and composition of connective tissue, his dissertation on the structure of cartilage and on chondrin being shortly followed by articles on bone and teeth.

His most valuable contributions were those to the physiological chemistry of the blood. It was early in these investigations that he discovered the peculiar property which many of the principles of the body possess, of rotating the plane of polarization. In a short paper published in 1857 he gives the results of investigations on the action of carbon dioxide on the blood, and concludes that the action of carbon dioxide on the coloring-matter of the blood renders it incapable of acting as a carrier of oxygen. After the researches of Stokes on the reduction of oxyhaemoglobin, Hoppe-Seyler explained in detail the action of carbon dioxide on blood, and devised a method for detecting blood containing carbon dioxide. Following up the line suggested by the work of Brewster and Herschel on the absorption bands formed in the spectrum of light which had been passed through various gases, Hoppe-Seyler studied the behavior of blood-coloring matter in the spectrum of sunlight, and published his celebrated paper on this subject. He concluded, from the investigation of the

absorption spectrum of blood, that haematin, which had been considered the blood-coloring matter, did not exist as such in the blood, but was formed as a product of decomposition. Stokes afterwards showed that the coloring-matter of blood exists in two states of oxidation, distinguished by difference in color and in the spectrum.

Hoppe-Seyler isolated the blood-coloring matter, and studied its composition, its combinations with oxygen and carbon dioxide, and its decomposition.

Only a slight idea of his energy can be gained from the articles published by him, as a large part of the work done under his direction appeared under the names of his pupils. In 1858 he published his "Handbook of Physiologico-Chemical and Pathologico-Chemical Analysis." This work has passed through six editions, the last having been published in 1893. He also published a "Text-book of Physiological Chemistry," and founded in 1877 the "Zeitschrift für physiologische Chemie," of which he has been the chief editor.

J. E. G.



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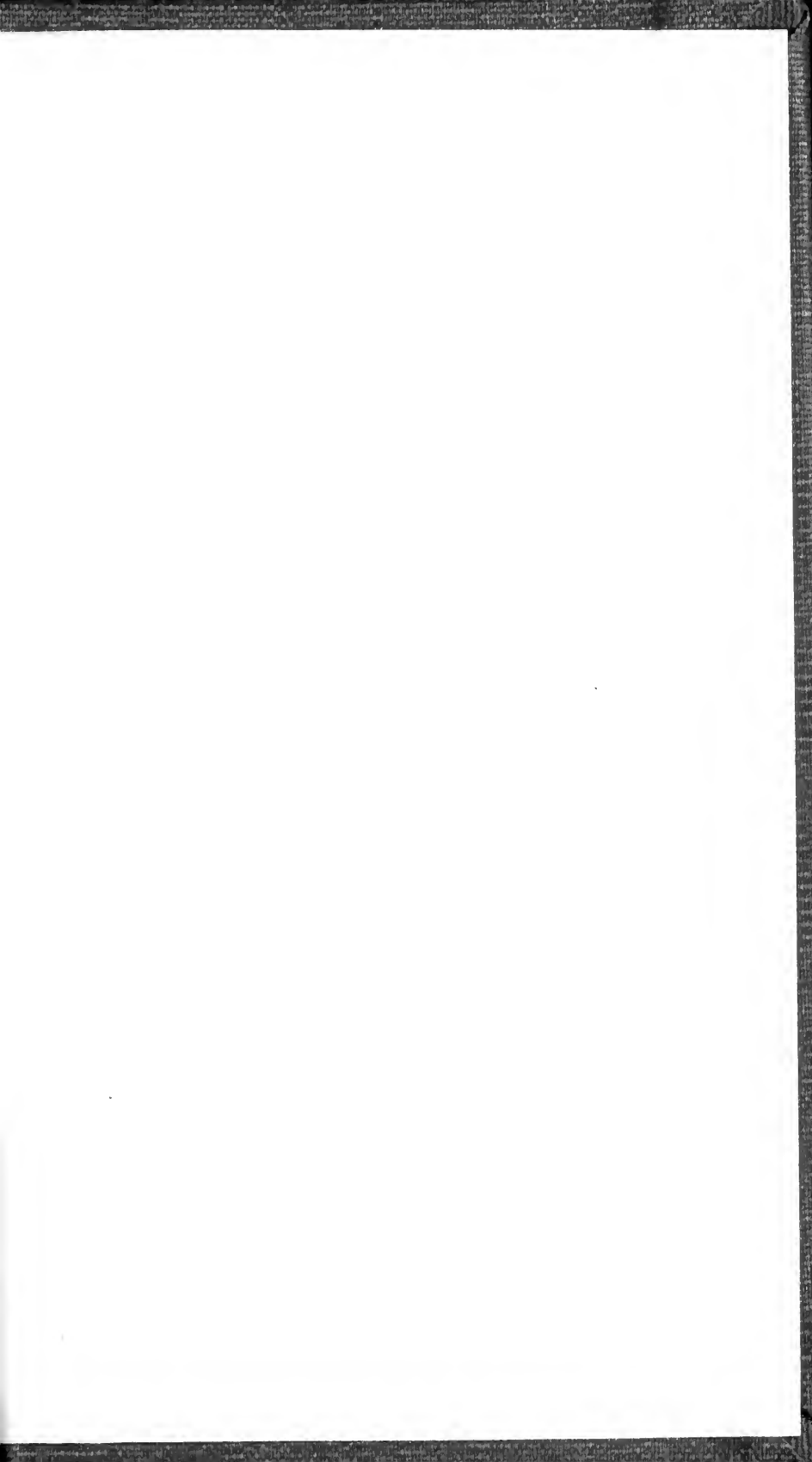
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